polymorphic forms each with a characteristic melting point. (Some, *e. g.*, 2-stearyldipalmitin, have only two.) Where, as in the case of SMS, four forms actually do occur to correspond with Malkin's four published m. p. values, new patterns should be expected, since only three of Malkin's four patterns appear to be authentic.

Ivorydale, Ohio Received January 3, 1949

[Contribution No. 89 from the General Laboratories of the United States Rubber Company]

Infrared Studies of 1,2- and *trans* 1,4-Structure of Polybutadiene and Butadiene–Styrene Copolymers Polymerized at Various Temperatures[1]

By E. J. Hart[2] and A. W. Meyer

One of the major improvements in the quality of synthetic butadiene rubbers has resulted from the use of low temperatures of polymerization. In particular, tensile strength, resilience, flex life, abrasion resistance and processing properties of tire tread stocks have been favorably affected.[3]

It is of great importance to determine the reasons for improvements in the physical properties of low temperature polymers in order to expedite future research. Comparison of the physical properties of Hevea rubber with isomerized rubber or synthetic polyisoprene illustrates the point that crystallizable polymers are required for high tensile strengths, particularly in gum vulcanizates. From the low tensile strengths obtained on isomerized rubber it may be concluded that the existence of random sequence of *cis–trans* configurations is sufficient to prevent crystallization during stretching of the rubber. Also in synthetic polyisoprene, polybutadiene and GR-S, appreciable quantities of 1,2-addition are found and become the source of further irregularities in the chain structure of the polymer. 1,2- and *cis–trans* 1,4-additions in random sequence may be considered as the major structural variations leading to noncrystallizable and inferior polymers. In order to determine the relative importance of 1,2- and *cis–trans* 1,4- addition, it is necessary to develop analytical methods for these isomeric units present in butadiene polymers.

Several methods have been employed in the determination of the amount of 1,2- addition in polybutadiene and butadiene–styrene copolymers. In emulsion polymers it has been reported that 78% of the butadiene addition is in the 1,4- configuration and the remainder in the 1,2- configuration.[4] Therefore, 78% of the butadiene is present as *cis–trans* isomers of the 1,4- addition product arranged in random sequence. From the results on isomerized rubber it would be expected that even if the 1,2- addition could be reduced to negligible values, inferior products would still result because of the presence of the large amount of *cis-trans* isomers in random sequence.

Beu, Reynolds, Fryling and Murry[5] reported that crystallization can be developed in polybutadiene prepared at 20° and lower. Further, they deduced from their X-ray work that the partially crystallized rubber corresponded to the *trans*-configuration. However, it is difficult to measure the *trans*-isomeric content of the polymer quantitatively or even relatively by X-ray methods. Ozonization,[6] perbenzoic acid[7] and infrared[8] methods have been applied to the measurement of the per cent. 1,2-addition in butadiene polymers. Of these methods the perbenzoic acid and infrared methods are in fair agreement.

The present paper shows that the infrared spectrometer is admirably suited not only to the measurement of 1,2-addition but also to the measurement of *trans*-1,4-addition in polybutadiene and butadiene–styrene copolymers. It is the purpose of this paper to describe briefly the 1,2- and *trans*-1,4-addition analytical methods and also to report results on the effect of temperature of polymerization and styrene content on 1,2- and *trans*-1,4-addition in butadiene polymerization and copolymerization.

Experimental

Materials.—Emulsion polymers used in this study are listed in Table I. These were secured from the following sources; the 14R and 26E series[9] were obtained from the Synthetic Rubber Laboratories, University of Akron; the J888-J949 series was obtained from the Synthetic Rubber Division, United States Rubber Company, Naugatuck, Connecticut; GR-S and GR-S10 were regular commercial materials.

Purification of Polymers.—Since it is desirable to use carbon disulfide solutions of the polymers for the infrared analysis, the following

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[1] This paper was presented before the High Polymer Forum at the St. Louis Meeting of the American Chemical Society, September 7, 1948.

[2] Present address: Argonne National Laboratory, Chicago, Ill.

[3] W. A. Schultze, W. B. Reynolds, C. F. Fryling, L. R. Sperberg and J. E. Troyan, *India Rubber World*, **117**, 739 (1948).

[4] R. F. Dunbrook, *ibid.*, **117**, 617 (1948).

[5] K. E. Beu, W. B. Reynolds, C.F. Fryling and H. L. Murry, *J. Polymer Sci.*, **3**, 465 (1948).

[6] Rabjohn, Bryan, Inskeep, Johnson and Lawson, This Journal, **69**, 314 (1947).

[7] I. M. Kolthoff and T. S. Lee, *J. Polymer Sci.*, **2**, 206 (1947); I. M. Kolthoff, T. S. Lee and M. S. Mairs, *ibid.*, **2**, 220 (1947).

[8] J. E. Field and D. E. Woodford, private communication to Office of Rubber Reserve, October, 1945.

[9] W. K. Taft, private communication to Office of Rubber Reserve, January, 1948.

purification method was used: 2 g. of the polymer was dissolved in 100 cc. of carbon disulfide and the solution filtered through 300-mesh silk gauze to remove gel. Methanol was added to the filtered solution until complete precipitation took place. The precipitated polymer was then evaporated to dryness at room temperature. During this evaporation process two or three additions of carbon disulfide were made in order to facilitate removal of methanol from the polymer.

Preparation of Solutions.—The polymer purified as described above and freed from methanol was dissolved in carbon disulfide and made up to concentrations of 3 to 4%. Care was necessary in the purification process to minimize the danger of gelation by keeping the temperatures and exposure to air as low as possible. 14R5, 14R6 and GR-S10 were not obtained gel-free and these polymers were analyzed in the partially gelled condition.

Spectroscopic Methods.—A Perkin–Elmer Spectrometer was used for infrared studies of polymer structure. Conventional infrared techniques were employed by R. R. Hampton of our Infrared Laboratory. Details of the procedure will be described in a separate paper. Measurements of the intensities of absorption were made in the 900–1000 cm.$^{-1}$ region using solutions of the polymer in carbon disulfide.

For measurement of 1,2-addition in butadiene polymers the absorption of the 910 cm.$^{-1}$ infrared band by the polymer solution was compared with the absorption by octene-1 of National Bureau of Standards grade.

Absorption of the 967 cm.$^{-1}$ infrared band was used to measure the per cent. *trans*-1,4-addition in butadiene polymers. *trans*-4-Octene obtained from the National Bureau of Standards was employed for calibration purposes.

A study[10] of the National Bureau of Standards Spectra[11] of *cis*-2-butene, *trans*-2-butene, *cis*-2-pentene and *trans*-2-pentene reveals the fact that the 967 cm.$^{-1}$ band is more strongly absorbed by the *trans*-isomers than by the *cis*-isomers. Figure 1 contains N.B.S. spectra of *cis*-2-pentene and *trans*-2-pentene and our measurement of *trans*-4-octene. In Fig. 2 our measurements of the spectra of *trans*-4-octene and polybutadiene are shown to have absorption peaks at 967 cm.$^{-1}$. Therefore, it is concluded that the 967 cm.$^{-1}$ band may be used to measure *trans*-1,4-addition in butadiene polymers.

Calibration.—The calibration curves are given in Fig. 3. The molar extinction coefficient of octene-1 is 155. The same value was used for the vinyl side-group resulting from 1,2-addition in polybutadiene.

Molar extinction coefficients of the 967 cm.$^{-1}$ band were determined for three *trans*-olefins. These results appear in the following table.

Olefin	Molar extinction coefficient ε
trans-4-Octane	132 ± 2
trans-3-Hexene	133 ± 2
trans-2-Hexene	157 ± 2

where $\epsilon = \log (I_0/I_t)/cd$
c = concentration in moles/liter.
d = thickness of solution in cm.
I_0, I_t = initial and transmitted light intensity, resp.

Here it is shown that *trans*-3-hexene and *trans*-4-octene have practically identical extinction coefficients whereas that of *trans*-2-hexene is somewhat higher. There is a possibility that the absorption by the *trans*-1,4-unit in butadiene polymers would be affected by adjacent styrene or 1,2-addition structures. Since these structures are present in relatively small amounts they are considered to have secondary influence. Hence we assume that the molar extinction coefficients of the 967 cm.$^{-1}$ bands of the *trans*-4-octene and the *trans*-1,4-unit in butadiene polymers are identical. The *trans*-1,4-calibration curve in Fig. 3 is based on this assumption.

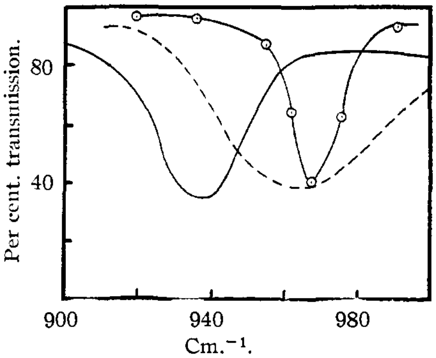

Fig. 1.—Infrared transmission curves for *cis*- and *trans*-2-pentene and *trans*-4-octene: —, *cis*-2-pentene, 10-cm. cell, 100 mm.; - - -, *trans*-2-pentene. 10-cm. cell, 39 mm.; O, *trans*-4-octene, CS_2, 30.15 g./l., 0.01045 cm. Curves for *cis*-2-pentene and *trans*-2-pentene determined from National Bureau of Standards Spectra 357 and 358, respectively, American Petroleum Institute Project 44.

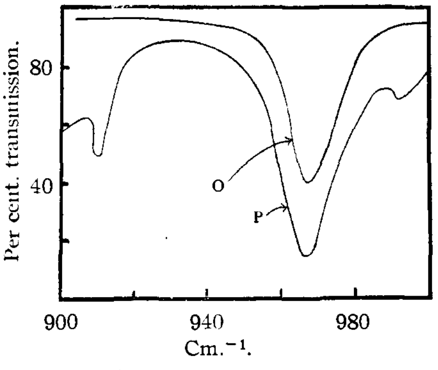

Fig. 2.—Infrared transmission curves for *trans*-4-octene and polybutadiene, cell length 0.01045 cm., CS_2 solvent: O, *trans*-4-octene, 30.15 g./liter; P, polybutadiene 26E77-96, 36.82 g./liter.

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[10] K. S. Pitzer, private communication.

[11] National Bureau of Standards Spectra Nos. 357, 358, 376 and 377, American Petroleum Institute Project 44.

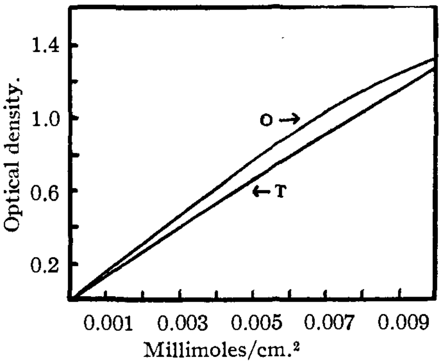

Fig. 3.—Calibration curves for 1,2- and *trans*-1,4-addition in butadiene polymers: O, 1,2-addition based on 1-octene; T, *trans*-1,4- based on *trans*-4-octene.

Results and Discussion

From the optical density of the band, concentration of polymer solution and thickness of the absorption cell, the per cent. 1,2- and *trans*-1,4-addition were calculated. Experimental results are given in Table I for butadiene–styrene copolymers and for polybutadiene polymerized at temperatures ranging from −19 to +97°.

Effect of Temperature of Polymerization on 1,2-Addition.—In Table I and Fig. 4 it is shown that the temperature of polymerization has a relatively small effect on 1,2-addition for polybutadiene and butadiene 71–styrene 29 copolymers. A maximum of 23.2% 1,2-addition exists at 50° which is in excellent agreement with the 23% found by Kolthoff, Lee and Mairs.[7] The amount of 1,2-addition decreases continuously with polymerization temperature to a value of 19.6% at −19°.

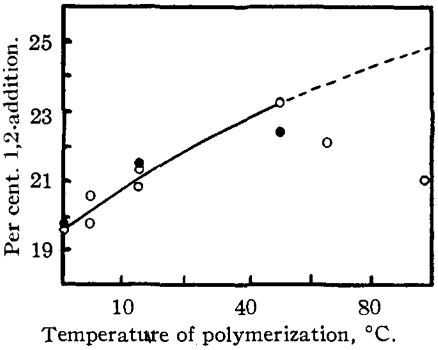

Fig. 4.—Effect of polymerization temperature on 1,2-addition in polybutadiene and 71/29 butadiene–styrene copolymers: O, polybutadiene; ●, 71/29 butadiene–styrene.

With reference to the polymers prepared at 65 and 97°, the spectra were run on samples that had partially gelled. The apparent decrease in 1,2-addition for these 65 and 97° polymers as the temperature is raised above 50° is interpreted as branching or crosslinking reactions that selectively attack the vinyl side-groups in polybutadiene. If we assume that 1,2-addition follows the dotted line in Fig. 4, for temperatures of polymerization beyond 50°, then 3.8 and 1.2% of the 1,2-addition product have reacted at polymerization temperatures of 97 and 65°, respectively. Further work on polymers prepared at temperatures above 50° is in progress to clear up this point.

A reduction in temperature of polymerization from 50 to −19° results in only a 3.6% decrease in per cent. 1,2-addition. This small change in per cent. 1,2-addition could hardly be expected to account for the considerable improvement in crystal-

TABLE I

ANALYTICAL DATA ON POLYBUTADIENE AND BUTADIENE–STYRENE COPOLYMERS

Polymer code[a]	Pol. temp., °C.	B/S charge ratio	n^{25}_D	% comb.[d] styrene	η_0 (CS_2)	% 1,2[b]	% 1,2 (cor.)	% trans[b]	% trans. (cor.)	1,4/1,2	Ratio $\frac{trans}{-cis}$
14R5	+97	100/0	1.5159	0.74	Gel	21.0	24.8[c]	51.4		3.03	2.16
14R6	+65	100/0	1.5156	0.37	Gel	22.1	23.8[c]	56.6		3.20	2.89
14R3	+50	100/0	1.5156	0.37	2.15	23.2		62.0		3.31	4.2
26E77-96	+ 5.5	100/0	1.5154	0.13	1.96	21.0		72.0		3.70	10.3
26E77-96	+ 5.5	100/0				21.6		71.4			
J946-4	+ 5	100/0	1.5148	−0.60	2.80	20.8	20.8	71.5		3.80	9.3
26E25-40	−10	100/0				19.8		74.8		4.05	13.9
26E41-56	−10	100/0	1.5144	−1.09	2.81	20.6		76.3		3.85	24.6
26E57-76	−19	100/0	1.5143	−1.22	1.02	19.6		79.6		4.10	100
J947-2	+ 5	95/5	....	3.8	2.60	20.2	21.0	68.6	71.3		
J948-B2	+ 5	90/10	1.5219	7.6	1.98	17.9	19.4	67.1	72.7		
J949-4	+ 5	85/15	....	12.7	1.72	18.4	20.9	64.9	73.8		
J888-3	+ 5	71/29	1.5344	23.3	2.11	16.1	21.0	58.3	76.1		
J889-3	−18	71/29	1.5352	24.3	3.16	14.8	19.6	63.5	83.9		
GR-S	+50	71/29	1.5345	23.4	2.08	16.8	21.9	49.6	64.8		
GR-S10	+50	71/29	1.5331	21.8	Gel	15.7		45.4			

[a] The 14R and 26E series of polymers were obtained from Government Laboratories, Univ. of Akron and the J series was obtained from U. S. Rubber Company, Synthetic Rubber Division, Naugatuck, Connecticut. 14R3, 14R5, 14R6, GR-S 10 and GR-S are made with persulfate formulas; the remainder of polymers are made with cumene hydroperoxide–Redox formulas. [b] An additional correction of −0.03X% styrene should be made for the absorption of combined styrene present in the copolymer. This is due to absorption of styrene at 910 and 967 cm.$^{-1}$. [c] See dotted line of Fig. 4. [d] Based on refractive index measurements and equations of Madorsky and Wood.[12] Actual % styrene in polybutadiene is zero.

lization and physical properties of butadiene polymers prepared at low temperatures.

Effect of Temperature of Polymerization on *trans*-1,4-Addition.—The *trans*-1,4-content of polybutadiene and 71/29 butadiene–styrene copolymers is given in Table I and shown in Fig. 5. It is found that *trans*-1,4- increases continuously from a value of 51.4% for the 97° polymer to 79.6% for the −19° polymer. This is a change of 28.2% and is considerably greater than the change of 3.6% found in 1,2-addition. Furthermore, the results indicate that at −19° substantially all of the 1,4-addition product is in the *trans*-form.

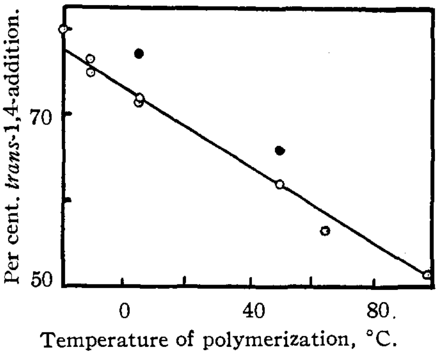

Fig. 5.—Effect of temperature of polymerization on *trans*-1,4-addition in polybutadiene and 71/29 butadiene–styrene copolymers: ○, polybutadiene; ●, 71/29 butadiene–styrene copolymers.

At 5° the ratio of *trans* to *cis* is 10.3, whereas at 50° it is 4.2. These changes should greatly enhance the ability of the polymer to crystallize on stretching, especially at low temperatures. This result has been demonstrated by the previously mentioned X-ray results.[5]

Effect of Combined Styrene.—Figure 4 also shows that the per cent. 1,2-addition in butadiene 71–styrene 29 copolymers decreases as the temperature of polymerization is lowered. A substantially identical decrease is observed for both polybutadiene and butadiene–styrene copolymers. The result indicates that the styrene unit has no influence in altering the ratios of 1,2- and 1,4-addition as polymerization temperatures are lowered. This is in agreement with the results of Kolthoff, Lee and Mairs[7] who employed the perbenzoic acid method for studying 1,2-addition.

In Fig. 5, the per cent. *trans*-1,4- in the butadiene 71–styrene 29 copolymers also is shown to increase with lowering of polymerization temperatures. The per cent. *trans*-1,4- is greater than that for polybutadiene. The correction for absorption at 967 cm.$^{-1}$ by styrene residues is −0.03% per % combined styrene. If this were applied to the values in Fig. 5, it would be insufficient to account for the differences from polybutadiene. It is possible that the adjacent styrene residues have some effect on the molar extinction coefficient of *trans*-1,4- configurations but suitable reference compounds are not now available for calibration purposes.

The influence of change from 0 to 23.3% combined styrene on 1,2- and *trans*-1,4-addition in butadiene–styrene copolymerization at 5° is shown in Table I. Figure 6 shows that 1,2-addition is independent of the styrene content when correction is made for the combined styrene in the copolymers. In Fig. 7 the *trans*-1,4- content is seen to increase with increasing combined styrene after correction for absorption at 967 cm.$^{-1}$ by the styrene residues. This effect was discussed in the previous paragraph.

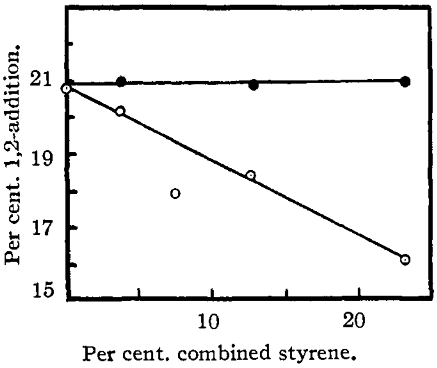

Fig. 6.—Effect of styrene on 1,2-addition in butadiene–styrene copolymers prepared at 5°: ○, uncorrected; ●, corrected for styrene content.

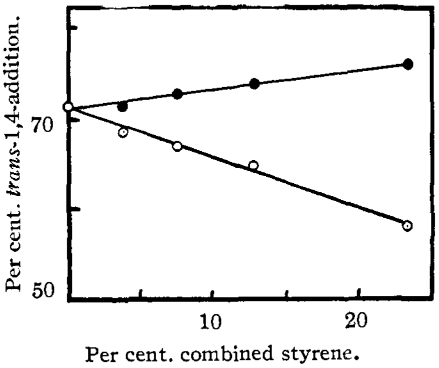

Fig. 7.—Effect of styrene on *trans*-1,4-addition in butadiene–styrene copolymers prepared at 5°: ○, uncorrected; ●, corrected for percentage of styrene.

The experimental results demonstrate that 1,2-addition decreases slightly and *trans*-1,4-addition increases considerably with decreasing temperature of polymerization. By far, the major effect of lowering polymerization temperature is this increase in the relative proportions of the *trans*-1,4- configuration in polybutadiene or butadiene–styrene copolymers.

Refractive Index of Polymers.—The refractive indices and intrinsic viscosities of the polymers used in these studies are given in Table I. The method used for refractive index is similar to that of Madorsky and Wood.[12] The refractive index of polybutadiene is shown to decrease with decreasing temperature of polymerization. Since the change is only about 0.3%, no correction was made in combined styrene determinations by the refractive index method on butadiene–styrene copolymers prepared at low temperatures.

Free Energy, Heat and Entropy of Activation. Since the 1,2-addition and *trans*-1,4-addition are known in these purified polymers, it is possible to estimate the per cent. *cis*-1,4-addition. One may then calculate the ratios of 1,4- to 1,2- and *trans*-1,4- to *cis*-1,4-addition products in these polymers. Figure 8 gives a plot of log$_e$ 1,4/1,2 *vs.* $1/T$. Figure 9 gives a plot of log$_e$ *trans* 1,4/*cis* 1,4 *vs.* $1/T$.

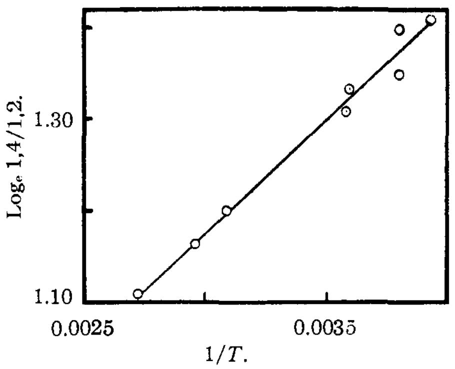

Fig. 8.—Log$_e$ of 1,4/1.2 *versus* $1/T$ in polybutadiene.

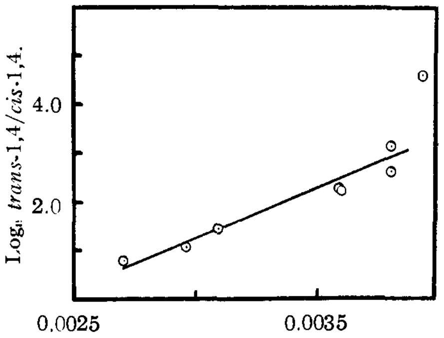

Fig. 9.—Log$_e$ *trans*-1,4/*cis*-1,4 *versus* $1/T$ in polybutadiene.

Having developed methods for the determination of per cent. 1,2- and *trans*-1,4- it is now possible to calculate differences between free energies of activation for 1,4- *vs.* 1,2- and *trans*-1,4- *vs.* *cis*-1,4-polymerization processes. Free radical propagation reactions in butadiene polymerization proceed through the formation of an intermediate allylic free radical. This radical is a resonance hybrid of the two forms

$$—CH_2—CH{=}CH—CH_2\cdot + —CH_2—\dot{C}H—CH{=}CH_2$$

Both the reaction leading to 1,4-addition and the reaction leading to 1,2-addition involve the same allylic radical and the same butadiene molecule if we neglect possible effects of the *cis*- or *trans*-configuration of the radical or butadiene molecule on the proportions of 1,2- and 1,4-addition. The reactions may be represented as

$$R—B\cdot + B \xrightarrow{k_{1,4}} R—B_{1,4}B\cdot$$
$$R—B\cdot + B \xrightarrow{k_{1,2}} R—B_{1,2}\,B\cdot$$

From studies carried out on the variation of the ratio of 1,4- to 1,2-addition with temperature of polymerization, the difference between the free energy of activation for 1,4- and 1,2-forms may be calculated. Results obtained are given by the equations

$$\Delta F^{\ddagger}_{1,4} - \Delta F^{\ddagger}_{1,2} = -480 - 0.88T$$
$$\Delta H^{\ddagger}_{1,4} - \Delta H^{\ddagger}_{1,2} = -480 \text{ cal.}$$
$$\Delta S^{\ddagger}_{1,4} - \Delta S^{\ddagger}_{1,2} = 0.88 \text{ E.U.}$$

Thus, the heat and entropy of activation favor 1,4-addition over 1,2-addition. However, both heat and entropy effects favoring 1,4-addition over 1,2-addition are very small.

The free radical polymerization of butadiene to yield *cis*- and *trans*-1,4-addition will next be considered. Butadiene exists in the S-*cis*- and S-*trans*-forms. (This means *cis* and *trans* with respect to the single bond of the butadiene.) Mulliken's calculations show a distinctly greater conjugation energy (2.5 kcal.) for the S-*trans*-form than for the S-*cis*-form.[13] Hence, the S-*trans*-form has greater stability, and lowering the temperature of polymerization will increase the concentration of S-*trans*-butadiene. Using the experimental ratios of *cis*–*trans*, free energies, heats and entropies of activation may be calculated for the following reactions

$$R\cdot + B_{c.t} \overset{k_1}{\text{———}} RB_t^{\cdot}$$
$$R\cdot + B_{c.t} \overset{k_2}{\text{———}} RB_c^{\cdot}$$

where $B_{c.t}$ refers to the equilibrium mixture of S-*trans*- and S-*cis*-butadiene. The results of calculations of differences between the *cis*- and *trans*-forms are given by the equations

$$\Delta F_t^{\ddagger} - \Delta F_c^{\ddagger} = -4200 + 10.2T$$
$$\Delta H_t^{\ddagger} - \Delta H_c^{\ddagger} = -4200 \text{ cal.}$$
$$\Delta S_t^{\ddagger} - \Delta S_c^{\ddagger} = -10.2 \text{ E. U.}$$

Thus, *trans*-1,4-addition has a 4.2 cal. lower heat of activation than the *cis*-1,4-. This advantage of a lower heat of activation is offset by an unfavorable entropy of activation. However, in the temperature range from −19 to 97°, the *trans*-1,4-form predominates, increasing with decreasing temperatures of polymerization.

Acknowledgment.—The authors wish to thank V. L. Burger, R. R. Hampton, and W. A. Hermonat for their assistance in carrying out the analytical work and purification of polymers.

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[12] I. Madorsky and L. A. Wood, private communication to Office of Rubber Reserve, September, 1944.

[13] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 265 (1942).

Summary

Infrared methods have been used in determining 1,2- and *trans*-1,4-addition in polybutadiene polymerized in the temperature range −19 to 97° and butadiene–styrene copolymers prepared at −18, 5 and 50°. *trans*-1,4-Addition increases and 1,2-addition decreases with decreasing temperature of polymerization. At −19°, substantially all of the 1,4-addition product is present in the *trans*-1,4-form. Approximately 20% 1,2-addition occurs at this temperature and is concluded to account for the major part of the non-crystallizable portion of polymers made at low temperatures. The influence of styrene on 1,2- and *trans*-1,4-addition in butadiene–styrene copolymers is also discussed. Free energy, heat and entropy of activation are calculated for 1,4- *vs.* 1,2-addition and *trans*-1,4- *vs.* *cis*-1,4-addition in the polymerization process.

PASSAIC, NEW JERSEY RECEIVED SEPTEMBER 23, 1948

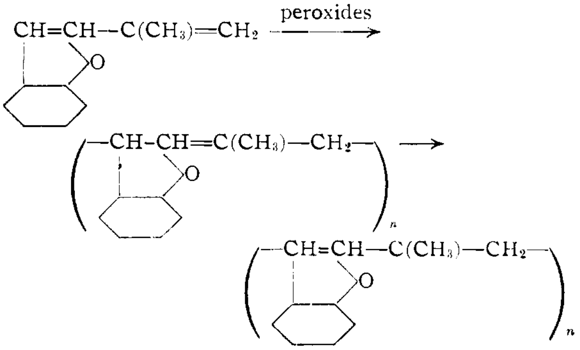
[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. VI. The Preparation of Vinyl Derivatives of Five-atom Heterocyclic Rings[1,2]

BY G. BRYANT BACHMAN AND LOWELL V. HEISEY[3]

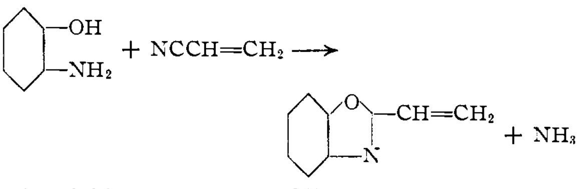
The preparation and polymerization of vinyl heterocyclic compounds of the thiophene[2c] and pyridine[2d] series have already been reported from this Laboratory. The present paper extends these studies to vinyl derivatives of other five-atom heterocyclic rings particularly in the furan and azole series.

2-Isopropenylfuran,[4] 2-isopropenyl-5-isopropylfuran and 2-isopropenylbenzofuran were prepared by dehydrating the tertiary alcohols obtained from the corresponding carboxylic acid esters and methylmagnesium halides. The dehydrations in the first two cases were very unsatisfactory with most dehydrating catalysts because of ring cleavages, but proceeded well (50–55% yields) on refluxing with sodium acetate and acetic anhydride. The dehydration of 2-(2′-hydroxy-2′-propyl)-benzofuran proceeded spontaneously on vacuum distillation to give the desired 2-isopropenylbenzofuran. The last compound is interesting because of its ability to polymerize alone with peroxide catalysts. It was pointed out previously[2b] that isopropenylbenzenes do not polymerize alone with peroxide catalysts, and in keeping with this 2-isopropenylfuran and 2-isopropenyl-5-isopropylfuran also do not polymerize alone with peroxide catalysts. 2-Isopropenylbenzofuran, however, is structurally related to coumarone which polymerizes by virtue of the active double bond of the furan ring. The isopropenyl compound probably behaves like a typical diene which accounts for its unusual ease of polymerization in the absence of comonomers.



All three of these vinylfurans copolymerized with butadiene to give rubbers.

A number of attempts were made to prepare vinyl derivatives of heterocyclic systems by condensing *o*-difunctional benzenes with vinyl compounds. 2-Vinylbenzoxazole was prepared in this manner from *o*-aminophenol and acrylonitrile or acrylic acid.



The yields were poor (14%); and other combinations were totally unsuccessful. Crotonic acid and *o*-aminophenol gave 2-methylbenzoxazole, a curious reaction first observed by Doeller.[5] Acrylic acid and *o*-phenylenediamine apparently gave a seven-atom ring compound (2-oxo-2,3,4,5-tetrahydro-1,5-benzodiazepine) instead of the desired 2-vinylbenzimidazole.

Preparations of 2-vinylbenzimidazole by other methods invariably led to polymers of this substance indicating its great readiness to polymerize. A group of substituted 2-ethylbenzimidazoles

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[1] From the Ph.D. thesis of L. V. Heisey, Purdue University, June, 1947. Read before the Organic Division at the St. Louis meeting of the American Chemical Society, September, 1948.

[2] For previous papers in this series see Bachman, *et al.*, THIS JOURNAL, (a) **69**, 2022 (1947); (b) **70**, 622 (1948); (c) **70**, 1772 (1948); (d) **70**, 2378 (1948); (e) **70**, 2381 (1948).

[3] Present address: McPherson College, McPherson, Kansas.

[4] Reichstein, Zschokke, Gehrig and Rona, *Helv. Chim. Acta*, **15**, 1118 (1932).

[5] Doeller, *Ber.*, **72B**, 2148 (1939).