Acknowledgment.—We wish to acknowledge the counsel and interest of Professor W. W. Beeman, in whose laboratory this work was carried out.

[CONTRIBUTION FROM THE B. F. GOODRICH COMPANY RESEARCH CENTER, BRECKSVILLE, OHIO]

The Radiation Induced *cis–trans* Isomerization of Polybutadiene. III[1]

BY MORTON A. GOLUB

RECEIVED FEBRUARY 2, 1960

A study was made of the γ-ray induced *cis–trans* isomerization of polybutadiene in solution and in the solid state, in the absence of any deliberately added sensitizer. Starting with an essentially all-*cis* or all-*trans* polybutadiene, the "unsensitized" isomerization approaches a radiostationary equilibrium in which the *cis/trans* ratio in the polymer is about 20/80, in contrast to the thermodynamic equilibrium ratio of 8/92 obtained in previous sensitized isomerizations of polybutadiene. The unsensitized reaction is first order in *cis* (or *trans*) content with a rate which is proportional to the radiation intensity. The isomerization in a 1% solution in benzene is about eight times as fast as that in the pure polymer. The G_0 values for the *cis* → *trans* reaction, *i.e.*, the number of *cis* double bonds initially converted to *trans* per 100 e.v. of energy absorbed by the polymer and the solvent, in the solution case, and by the polymer alone, in the solid state case, are about 1.2 and 14.6, respectively. The corresponding G'_0 values for the *trans* → *cis* reaction are about 0.3 and 3.6, respectively. The mechanism of the unsensitized isomerization is believed to involve excitation of the π electrons of the polymer double bonds to an antibonding state where free rotation, and hence geometric interconversion, can occur. This excitation, in the solid state, presumably results from collisions of energetic electrons with the polymer molecules: the double bond electrons are excited directly and/or indirectly through intramolecular energy transfer from the methylenic groups in the polymer. These processes occur also in solution but are less important there than intermolecular energy transfer from excited or ionized solvent molecules to the polymer double bonds.

Introduction

The radiation induced *cis–trans* isomerization of polybutadiene in benzene sensitized by bromine atoms or thiyl radicals was described in two previous papers.[2,3] The existence of an "unsensitized" isomerization in solution, *i.e.*, where no particular sensitizer was deliberately added to the polybutadiene prior to γ-irradiation, was briefly mentioned. It also was pointed out[2] that no evidence had yet been found for an analogous isomerization of the pure polymer in the solid state. Such a reaction could be expected on the basis of possible direct excitation of the polymer molecules, and hence also the π electrons of the double bonds, through impact with the Compton and secondary electrons generated by the γ-rays. Since the unsensitized isomerization of polybutadiene was considered to be a potentially very useful reaction for investigating energy transfer processes in irradiated polymers, it was desirable to re-examine the solid state irradiation of polybutadiene and at the same time obtain further data on the unsensitized isomerization in solution.

Recently it has been found that the pure polybutadiene can indeed undergo isomerization on γ-irradiation in the solid state. The rate is only about one-eighth of that in the unsensitized solution case which is itself very slow compared to the sensitized isomerizations considered previously. Nevertheless, the unsensitized isomerization, in solution or in the solid state, turns out to be a highly efficient non-chain reaction when viewed from the standpoint of energy utilization. Furthermore, both of these unsensitized isomerizations, starting from either the all-*cis* or all-*trans* polybutadiene, approach a radiostationary equilibrium in which the *cis/trans* ratio is about 20/80, in contrast to the thermodynamic equilibrium value of about 8/92 obtained in the sensitized isomerizations. This clearly indicated a fundamental difference between the mechanisms of the sensitized and unsensitized isomerizations, quite apart from the role of the sensitizer itself. The present work is therefore concerned also with elucidating this difference, which presumably is due to the sensitized isomerization proceeding through a transitory radical adduct whereas the unsensitized isomerization must involve an excited state of the polymer double bond.

Experimental

Two polybutadiene samples were used in this work, one having the monomer units arranged in a nearly all-*cis* configuration (CPB) and the other in a nearly all-*trans* configuration (TPB). The polymers were prepared by stereospecific polymerization techniques to a viscosity average molecular weight of around 400,000 for the *cis* polymer and around 150,000 for the *trans* polymer. The structures of the polybutadienes, as determined by infrared analysis, consisted of approximately 95% *cis*-1,4 and 2% *trans*-1,4 units in CPB, and about 95% *trans*-1,4 and 2% *cis*-1,4 units in TPB, with the remaining unsaturation in either polymer made up of vinyl groups resulting from 1,2- addition polymerization. Since the 1,2 units were not involved in the isomerization, only the percentage of the total 1,4 polymerization units having the *cis* (or *trans*) configuration, or, alternatively, the *cis/trans* ratio, in the polymer before and after irradiation was required. The *cis/trans* ratios of CPB and TPB were thus taken to be 98/2 and 2/98, respectively.

Stock solutions of CPB in benzene, with and without antioxidant, and of TPB in benzene-d_6, without antioxidant, were prepared for γ-irradiation to a polymer concentration of about 10 g./l. Additional solutions of CPB in benzene at concentrations up to about 18 g./l. as well as solutions of this polymer in toluene, *m*-xylene, ethylbenzene and tetralin, also were employed. It was necessary to carry out the solution isomerization in an aromatic solvent since the polybutadiene gels on γ-irradiation in aliphatic, cycloaliphatic or other solvents and thus cannot be recovered in a form suitable for infrared analysis. However, on irradiation in benzene or toluene, the polymer undergoes considerable phenylation which, while not affecting the isomeri-

---

[1] A portion of this material was presented at the 125th Meeting of the American Association for the Advancement of Science, Washington, D. C., December, 1958. Work was accomplished under Air Force contract, the sponsoring agency being the Materials Laboratory of Wright Air Development Center.

[2] M. A. Golub, THIS JOURNAL, **80**, 1794 (1958).

[3] M. A. Golub, *ibid.*, **81**, 54 (1959).

zation kinetics, does complicate the infrared analysis. This complication arises because the attached phenyl groups absorb in the same range of the infrared as do the *cis* double bonds, making it difficult or impossible to determine the *cis/trans* ratio in polybutadienes irradiated to high enough doses where the phenylation is quite pronounced. In order to obtain a definitive estimate of this ratio for the radiostationary state in benzene, a few experiments also were carried out on CPB in benzene-d_6. Since the deuterio phenyl groups formed from this solvent absorb at much higher wave lengths in the infrared than the ordinary phenyls, they do not interfere with the *cis/trans* determination. The solvents were all commercially available C.P. materials; the benzene-d_6 was purchased from Merck and Co., Ltd., Montreal, Canada.

In the solution isomerization case, portions of the stock solutions were placed in ordinary screwcap glass bottles and irradiated in air at room temperature. Aliquots of the irradiated solutions were withdrawn after receiving the desired doses, and the polymers contained therein analyzed for *cis/trans* ratio by means of infrared absorption spectra run on thin films cast from these solutions. In the solid state case, polymer films were prepared directly from the stock solutions onto rock salt plates, the spectra of the polymers then run, after which the plates were sealed in glass cells *in vacuo* and irradiated to a series of doses at room temperature. Following each successive dose, the salt plates were removed from the cells, the spectra of the irradiated polymers obtained and the plates then re-sealed *in vacuo* for further irradiation until integrated doses in excess of about 300 megaroentgens were received. The irradiations were performed in either of two Co^{60} γ-ray sources having radiation fluxes initially of about 0.08 and 0.14 Mr./hr., with the latter intensity later increased to about 0.43 Mr./hr.

The infrared method of determining the *cis/trans* ratio in the polybutadienes, which was based on the characteristic absorption bands for the *cis* and *trans* double bonds at 13.6 and 10.35 μ, respectively, was described previously.[2,3] The spectra of CPB and TPB were presented in the first paper of this series[2] and need not be given here. Except for showing some phenylation in the case of CPB and occasionally a small amount of oxidation in either polymer, the spectra of the irradiated polymers were similar to those of the corresponding unirradiated ones except for changes in the *cis* and *trans* content. Phenylation shows up as a strong band at 14.4μ and a weaker one at 13.3μ, indicating the presence of monosubstituted phenyl groups attached to the polymer chain. These bands are similar to those found in the polystyrene spectrum at the same wave lengths.[4] A sharp peak at 13.6μ (over and above the regular *cis* band centered at this wave length) also occurs in the spectra of the phenylated polymers which may be due to two phenyl groups attached to the same carbon atom alpha to the double bond. At relatively low doses, the extent of phenylation in CPB is slight, and the interference of the phenyl peaks with the *cis* band located in the 13–15μ region can be practically ignored. However, at higher levels of phenylation, it is very difficult to estimate the absorption due to the *cis* structure itself. This difficulty is especially pronounced in the case of TPB where just a small amount of phenylation overlaps considerably any *cis* structure which might have been formed during γ-irradiation. Consequently, work in benzene or toluene was confined to CPB at fairly low doses (less than 30–40 Mr.), while benzene-d_6 solutions of CPB and TPB were used for much higher doses.

The solution irradiations had to be carried out in air since the polymer usually commenced to gel after a dose of about 10–20 Mr. when irradiated in nitrogen or other inert atmosphere. Furthermore, even in air irradiations, it was necessary to work at polymer concentrations less than about 20 g./l. in order to avoid rapid crosslinking which set in at the higher concentrations. Although the molecular weight of the polymers in dilute solution dropped somewhat on irradiation in air, the infrared spectra of the recovered polymers were usually acceptable. In the absence of antioxidant, some oxidation of the polymer occurred, but neither it nor phenylation nor chain scission affected the rate of the solution isomerization. The solid state isomerizations were carried out *in vacuo* so as to avoid oxidation of thin polymer films which results in poor spectra. Since the antioxidant exerted a marked inhibiting effect on the solid state isomerization, such work was confined to the antioxidant-free stock solutions. A detailed study of the mechanism of this inhibition by various antioxidants and the so-called antirads is contemplated.

Results

TABLE I

RADIATION INDUCED ISOMERIZATION OF POLYBUTADIENE

Solvent	Polymer concn., g./l.	Dose rate, Mr./hr.	Total dose, Mr.	% *trans* in CPB	10^9k, r.$^{-1}$	G_0[b]
			cis-Polybutadiene			
None	...	0.410	117.0	10.9	0.83	
	...	.383	304.6	22.4	.83	
	...	.135	284.6	21.0	.79	
	...	.085	22.1	4.0	.82	
				Av.	0.82 ± 0.02	$14._6$
Benzene	10.2[a]	.421	27.9	17.2	6.1	
	9.5	.421	27.9	19.0	7.1	
	17.6[a]	.141	10.0	8.6	7.3	
	8.8[a]	.141	10.0	9.1	7.6	
	10.2[a]	.078	22.5	12.7	5.3	
	4.1[a]	.078	22.5	14.1	6.0	
				Av.	6.6 ± 0.9	1.2_1
Toluene	9.1[a]	.422	20.0	13.0	6.1	
	10.7	.422	20.0	14.8	7.1	
	9.1[a]	.141	15.0	11.0	6.3	
	9.1[a]	.082	15.7	9.5	5.2	
	11.0	.082	15.7	11.3	6.3	
				Av.	6.2 ± 0.7	1.1_4
m-Xylene	9.2[a]	.079	22.5	10.8	4.3	0.7_8
Ethylbenzene	12.4[a]	.406	18.6	9.0	4.1	0.7_5
Tetralin	10.6[a]	.392	45.6	11.6	2.3	0.4_2
Benzene-d_6	10.8[a]	.382	99.4	46.4	6.8	
	10.8[a]	.382	185.6	63.4	6.7	
	10.8[a]	.381	265.0	71.7	6.8	
				Av.	6.8 ± 0.1	1.2_4
			trans-Polybutadiene			
				% *cis* in TPB	$10^9k'$, r.$^{-1}$	G_0'[b]
None	...	0.390	282.7	6.5	0.20	3.5_9
Benzene-d_6	10.2	.382	99.4	11.4	1.6	
	10.2	.382	185.6	15.1	1.4	
	10.2	.381	265.0	17.3	1.5	
				Av.	1.5 ± 0.1	0.2_8

[a] With antioxidant. All other runs were carried out in the absence of antioxidant. [b] Calculated on the basis of a 1% polymer solution by weight in the solution isomerization case.

Some representative kinetic data for the γ-ray induced unsensitized isomerization of CPB and TPB in solution and in the solid state are given in Table I. The first order rate constants, k and k', representing the forward and reverse processes, respectively, of the radiochemical isomerization reaction

$$cis \underset{k'}{\overset{k}{\rightleftharpoons}} trans \qquad (1)$$

were calculated using the expressions

$$k = \frac{-2.303K}{(1+K)} \times \frac{\mathrm{d}\log(1 - x/x_e)}{\mathrm{d}R} \qquad (2)$$

$$k' = \frac{-2.303}{(1+K)} \times \frac{\mathrm{d}\log(1 - y/y_e)}{\mathrm{d}R} \qquad (3)$$

K is the equilibrium constant for reaction 1, x is the per cent. *cis* changed into *trans* after a radiation dose R and x_e is the maximum per cent. *cis* which can be converted in this reaction, starting with CPB, while y and y_e are the corresponding amounts

---

(4) For a representative infrared spectrum of polystyrene, see E. K. Plyler and C. W. Peters, *J. Research Natl. Bur. Standards*, **45**, 462 (1950).

of *trans* which can be changed into *cis*, starting with TPB. Since the *cis/trans* ratios of CPB and TPB were initially 98/2 and 2/98, respectively, and approached the radiostationary value of about 20/80, K was assumed to be 4.0, and x_e and y_e were taken to be 78 and 18%, respectively. The logarithmic terms in the above expressions were determined from the slopes of the various kinetic plots obtained, such as those depicted in Fig. 1.

As seen in the figure, the data for CPB in benzene at relatively low doses (less than about 40 Mr.) are completely compatible with those obtained in benzene-d_6, so that the latter solvent could be regarded, at least from the standpoint of promoting the isomerization of polybutadiene, as equivalent to ordinary benzene. There was no evidence of an isotope effect in the rates of isomerization in these two solvents. At higher doses phenylation of CPB in benzene becomes serious enough that the calculated *cis/trans* ratios turn out to be greater than they should be. This is illustrated by the dotted line in Fig. 1.

Of the various aromatic solvents considered (Table I), benzene and toluene were found to be the most effective, with nearly equal ability in promoting the solution isomerizations. *m*-Xylene and ethylbenzene are less effective in this respect, having rate constants about two-thirds as large as those of benzene and toluene, while tetralin was even still less effective, with a rate constant only about a third as large as those for benzene and toluene. Some work with cumene, not given in the table, indicated a very small but finite amount of isomerization with a rate constant of the order of about twice that of the pure polymer in the solid state. The essential feature of all the solvents promoting the isomerization of CPB is, of course, the presence of the benzene ring in the molecule of the given solvent. Furthermore, the first four solvents in Table I along with cumene comprise a series of aromatic compounds for which the solution isomerization rate decreases more or less regularly with increasing amount of carbon atom substituents attached to the ring. This decrease in rates is greater than would be expected on the basis of a decrease in the electron fraction of the benzene ring in the solvent molecules. The observed trend in isomerization rates may have to do with the relative extents to which excitational energy originally located in the benzene nucleus of these compounds is dissipated through intramolecular transfer out of the ring into the substituents, thereby affecting the relative amounts of energy available for transfer to the polymer molecules, and hence for isomerization.

The results presented in Table I reveal that the polymer concentration and the presence or absence of antioxidant have very little effect on the rate constant for the solution isomerization. Actually, however, there is a slight increase in rate with dilution, but to see this necessitates carrying out the various concentration runs repeatedly and under identical conditions. The data also show that k (and presumably also k') is independent of the dose rate. Since $I\mathrm{d}t$ may be substituted for $\mathrm{d}R$ in expressions 2 and 3, the time rate of isomerization, $-\mathrm{d}(cis)/\mathrm{d}t$ (or $-\mathrm{d}(trans)/\mathrm{d}t$), in addition to being first order in *cis* (or *trans*) content, is proportional to the radiation intensity I. The energy yields G_0 and G'_0 represented the number of *cis* or *trans* double bonds initially isomerized per 100 e.v. absorbed by both polymer and solvent, in the solution case, and by the polymer alone, in the solid state case. In calculating these yields, it was assumed that a dose of one megaroentgen corresponded to an absorption of 6.08×10^{19} e.v./g. by either the polymer solution or the pure polymer film.

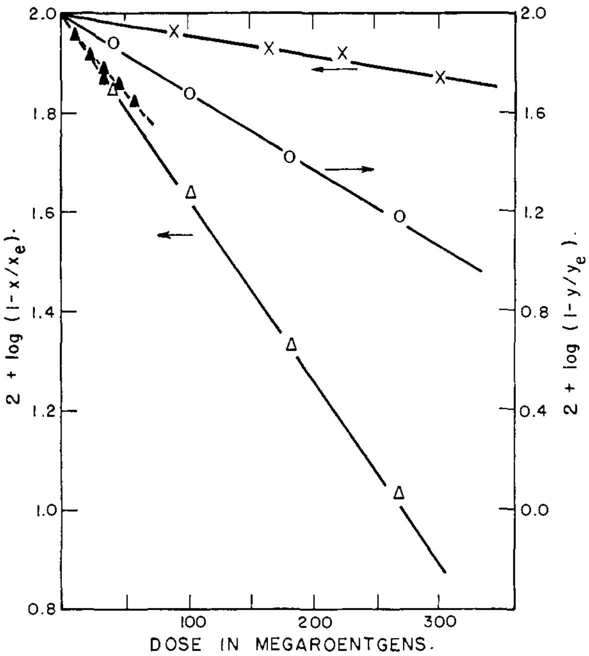


Fig. 1.—Kinetic plots of the radiation induced isomerization of polybutadiene: ▲, CPB in benzene; △, CPB in benzene-d_6; ○, TPB in benzene-d_6; ×, CPB in the solid state.

Discussion

Efficiency of the Solution Isomerization.—The G_0 values for the isomerization of CPB in a 1% solution by weight in benzene and in the solid state were found to be about 1.2 and 14.6, respectively. Inasmuch as the former value is based on the energy absorbed by the entire solution, if no energy transfer occurred between solvent and polymer molecules, the effective energy yield in the 1% benzene solution would be around 120 when calculated in terms of the energy absorbed only by the polymer. But the pure polymer gave a yield of only one-eighth this value, so that energy must be transferred from the solvent to the polymer in order for the solution isomerization to have such a high effective yield. Since the fate of much of the ionizational and excitational energy produced on γ-irradiation is to end up in low lying excited states,[5] part of the energy transfer from solvent to polymer could well proceed from the benzene triplet (3.6 e.v.)[6] to the low lying triplet state of

---

(5) M. Burton, *J. Chem. Educ.*, **36**, 273 (1959).

(6) H. Shull, *J. Chem. Phys.*, **17**, 295 (1949).

the vinylene unit (3.2 e.v.).[7] On an energy basis, charge transfer as well as transfer between higher excited states also could be involved here since benzene and the olefinic groups in the polymer have similar ionization and excitation potentials.[8] In this case, as a result of very rapid internal conversion processes ($\sim 10^{-13}$ sec.)[9] affecting highly excited states whether formed directly or through neutralization of ions, the result may again be a low lying excited state of the olefinic group as the precursor in the isomerization. At any rate, the net energy transfer to the polymer molecules in benzene is seen to be of the order of some seven times the energy acquired by the polymer solute directly on γ-irradiation. This is not an unreasonably large value to find for the extent of energy transfer in view of the sensitized fluorescence studies of Kallmann and Furst.[10] It should be noted in passing that the G_0 value for the isomerization of CPB in benzene obtained in the present work (1.21) is higher than that reported earlier[2] (0.92). This new value is considered to be more accurate since it is based on more extensive and refined experiments.

The G'_0 values obtained for the isomerization of TPB in benzene-d_6 and in the solid state (0.28 and 3.59, respectively) are only about one-fourth the corresponding values for CPB isomerization. This arises from the fact that, since $k/k' = 4$, a *trans* double bond, after excitation to a higher energy level in which free rotation can occur and subsequent return to the ground state with reestablishment of the double bond, has only one-fourth the chance of being converted to the *cis* configuration as remaining in the *trans* form.

Efficiency of the Solid State Isomerization.—In addition to showing considerable energy transfer from solvent to solute in the solution isomerization of CPB or TPB, this work demonstrates that the solid state isomerization of polybutadiene involves a highly efficient utilization of the energy introduced in the system on γ-irradiation. Thus, in the case of CPB, 14–15 double bonds are isomerized initially for every 100 e.v. absorbed in the pure solid polymer, or one double bond for about every 7 e.v. absorbed *anywhere* in the system. Since the methylenic and olefinic groups in the polymer $[(\text{—CH}_2\text{—CH}{=}\text{CH—CH}_2\text{—})_n]$ can be considered to absorb *directly* approximately equal amounts of the radiant energy, the effective energy yield, in the absence of intramolecular energy transfer, would then be one *cis* double bond isomerized for each 3.5 e.v. directly absorbed by the olefinic groups. Although this energy is sufficient to excite the double bond to a triplet state ($\sim$3.2 e.v.)[7] and hence sufficient for isomerization, the indicated yield is much too high to be accounted for without invoking energy transfer processes in the polymer molecule; it demands that virtually all the energy absorbed directly by the vinylenes be used in the isomerization. This is impossible, of course, since the energy imparted to the system on γ-irradiation is not deposited in quanta of just 3.5 e.v., but rather over a range of 10–15 e.v. on down. Thus, transfer of ionizational and/or excitational energy from the methylenic groups to the adjacent vinylene groups must occur to a very important extent. Such transfer processes are quite probable inasmuch as both the ionization and excitation potentials of the olefinic groups are lower than the corresponding ones for the methylenic groups.[11]

In determining the fate of the energy absorbed by CPB in the solid state case, apart from the efficient isomerization, it is necessary to take into account only the minor factor of crosslinking (and concomitant hydrogen production), since no other important structural changes occur on γ-irradiation. In particular, there is no perceptible decrease in either the vinyl or vinylene content in CPB up to quite high doses (150 Mr.), although some vinylene disappearance was observed in TPB. Vinyl decay in polyethylene is well-known,[12] and vinylene decay in *cis* or *trans* polybutadiene in the presence of polyethylene recently has been reported.[13] Further work on the subject of vinylene disappearance in polybutadiene is in progress here but, for the present, this factor will be disregarded. Consider, now, the energy requirements for the processes ensuant on absorption of 100 e.v. by CPB in the solid state. The energy required to form a crosslink is just that required to break a C–H bond (4.2 e.v.) since the subsequent steps leading to the formation of a crosslink and a molecule of hydrogen are exothermic and so no additional energy is needed.[13] For a G-value of crosslinking $G(\text{X})$[14] of about 3.6, approximately 3.6×4.2 or 15.1 e.v. is consumed in this reaction. Also, if the isomerization proceeds through the 3.2 e.v. triplet state of the vinylene group, the energy thus consumed would be $5/4 \times 14.6 \times 3.2$ or 58.4 e.v. The 5/4 factor takes into account the one out of five excited *cis* units which remains as *cis* after return to the ground state. The isomerization and crosslinking reactions thus account for at least 73.5 e.v. out of the total 100 e.v. absorbed. If higher excited states of the vinylenes also take part in the isomerization, an even larger fraction of the total energy input would then be accounted for. It is thus evident that the solid

---

(7) K. J. Laidler, "The Chemical Kinetics of Excited States," Oxford, 1955, p. 95.

(8) Thus, for example, benzene has an ionization potential of 9.25 e.v. [P. G. Wilkinson, *J. Chem. Phys.*, **24**, 917 (1956)] and an excitation potential of about 6.76 e.v. (very strong singlet) [R. Pariser, *ibid.*, **24**, 250 (1956)] while the vinylene group has an ionization potential of about 9.27 e.v. (as in *trans*-butene-2) [R. E. Honig, *ibid.*, **16**, 105 (1948)] and an excitation potential of about 6.5 e.v. [E. P. Carr and H. Stücklen, *ibid.*, **4**, 760 (1936); THIS JOURNAL, **59**, 2138 (1937)].

(9) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

(10) H. Kallmann and M. Furst, *Phys. Rev.*, **79**, 857 (1950); *ibid.*, **81**, 853 (1951); M. Furst and H. Kallmann, *ibid.*, **94**, 503 (1954).

(11) Thus, *e.g.*, according to W. C. Price, *ibid.*, **47**, 444 (1935), the ultraviolet absorption of ethane commences at about 1350 Å. while that of ethylene commences at about 1740 Å. The latter absorption corresponds roughly to the 6.5 e.v. state discussed by Carr and Stücklen (ref. 8). On the other hand, the methylenic group has an ionization potential which is certainly not less than 10.2 e.v. [G. G. Hall, *Trans. Faraday Soc.*, **50**, 319 (1954)] whereas the vinylene unit has an ionization potential of about 9.3 e.v. (Honig, ref. 8).

(12) See, for example, M. Dole, D. C. Milner and T. F. Williams, THIS JOURNAL, **80**, 1580 (1958).

(13) T. F. Williams and M. Dole, *ibid.*, **81**, 2919 (1959).

(14) E. Witt, *J. Polymer Sci.*, **41**, 507 (1959). Actually this $G(\text{X}) \sim 3.6$ is the value obtained for an emulsion polybutadiene which has a low *cis/trans* ratio ($\sim$1/5) and considerable vinyl unsaturation, and therefore it may not be quite the same for CPB. However, this value will have to serve for the present, in the absence of a precise determination of $G(\text{X})$ for CPB, but it is perhaps not very different from the true value for this polymer.

state isomerization of CPB is a highly efficient reaction when viewed from the standpoint of energy utilization.

Mechanism of Isomerization.—The results of the "unsensitized" *cis–trans* isomerization of polybutadiene thus have been interpreted in terms of an energy transfer mechanism. Such a mechanism is consistent with the observed dependence of the isomerization kinetics on the first power of the radiation intensity as well as the reaction being first order in isomerizing species. The mechanism involves, in the solid state case, the direct as well as indirect excitation of the π electrons of the double bonds through collisions between polymer molecules and the energetic electrons generated by the γ-rays. Energy acquired by the methylenic groups is, for the most part, transferred intramolecularly into the double bonds. In the solution case, such processes also occur but they are much less important there than collisions of the second kind between the polymer double bonds and excited solvent molecules. The essential feature of the energy transfer mechanism is that the double bond is excited to a higher energy level in which the electrons are no longer involved in bond formation (the so-called antibonding state) so that free rotation is then possible about the remaining single σ bond connecting the carbon atoms of the original double bond. On return of the antibonding state to the ground state with release of its excitational energy, the double bond is re-established, but with the *trans* form predominating, although not to quite the same extent as in the sensitized case.[2,3]

The mechanisms for the two types of isomerization are, therefore, fundamentally different in that the sensitized reaction involves the formation of a transitory radical adduct whereas the unsensitized isomerization takes place *via* an excited state of the polymer double bond. This difference in mechanism may be responsible for the ultimate *cis/trans* ratio being higher in the unsensitized case (20/80) than in the sensitized one (8/92). In the latter case thermodynamics must determine the value of this ratio, but in the former case the relative populations of the *cis* and *trans* forms in the higher energy levels probably determine the final value of the *cis/trans* ratio.[15] Thus, while the more stable form predominates in a thermodynamic equilibrium, the less stable form is often favored in a system exposed to strong illumination.[16] Examples of systems showing differences of this kind between the values of the *cis/trans* ratio for thermodynamic and photostationary equilibria are the maleic acid–fumaric acid interconversion[17,18] and the dibromoethylene isomerization.[19] Although no prediction can be made about the *cis/trans* ratio in a given system exposed to γ-rays, it may be that the concentration of the less stable isomeric form will likewise be higher in the radiation case than in the thermal one, and this is what has been found for polybutadiene. In view of the fact that Kailan[20] obtained the same ratio in the isomerization of maleic or fumaric acid whether the system was exposed to the penetrating rays from radium or to mercury light, it would be interesting to find out whether ultraviolet irradiation of polybutadiene (in the absence of a sensitizer) would give a ratio similar to that obtained here with γ-rays. Unfortunately, however, the photochemical analog of the radiation induced *unsensitized* isomerization of polybutadiene has not been accomplished, so that this notion could not be tested.

The possible participation of "sub-excitation" electrons in the unsensitized isomerization needs to be considered. Platzman[21] has estimated that such electrons are responsible for about 20% of the total energy absorbed on irradiation. Since the energy required to excite the vinylene group to its lowest triplet state is about 3.2 e.v., if all the sub-excitation electrons were somehow employed in the isomerization and these were the sole means for promoting this reaction, the maximum G value in the solid state case would be about 6, whereas the value obtained for CPB is 14.6. Thus, sub-excitation electrons cannot play an important role in the solid state isomerization. On the other hand, such electrons may be quite important in the solution isomerization case. Since the lowest excitation potential of benzene is 3.6 e.v., there will be many electrons with energy ϵ in the range $3.2 < \epsilon < 3.6$ and thus capable of exciting the vinylene groups in the polymer. If only one out of every five sub-excitation electrons produced in the benzene solution of CPB manages to reach a vinylene group and still have energy in the indicated range, the observed yield of 1.2 in the solution isomerization could be entirely accounted for. It appears, therefore, that sub-excitation electrons may well play an important role in the solution isomerization case, if not a major one.

It might be thought that part of the observed *cis–trans* isomerization in CPB could have resulted from a double bond migration such as

$$—CH_2—CH{=}CH—CH_2— \rightsquigarrow —\dot{C}H—CH{=}CH—CH_2— \rightleftarrows —CH{=}CH—CH—CH_2—$$

$$—CH{=}CH—CH—CH_2— + H \longrightarrow —CH{=}CH—CH_2—CH_2—$$

Any new double bonds formed in this way would be assumed to be predominantly in the *trans* configuration and so give rise to an apparent isomerization in contradistinction to a genuine *cis-trans* isomerization of a particular double bond. Infrared analysis could not, of course, differentiate between these two processes in the case of CPB. However, some very preliminary work with a high *cis* polybutadiene-2,3-d_2 (DCPB) showed quite definitely that migration does not occur to any significant extent. On γ-irradiation of this polymer $[(—CH_2—CD{=}CD—CH_2—)_n]$ in the solid state, only a trace of *trans* —CD=CH— units was formed, which could arise from double bond migration, whereas there was considerable formation of *trans* —CD=CD— units through isomerization

---

(15) A. R. Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

(16) L. Crombie, *Quart. Rev.*, **6**, 101 (1952).

(17) A. Kailan, *Z. physik. Chem.*, **87**, 333 (1914).

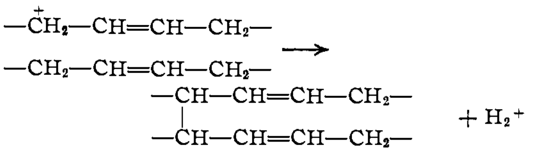
(18) K. Höjendahl, *J. Phys. Chem.*, **28**, 758 (1924).

(19) A. R. Olson and W. Maroney, THIS JOURNAL, **56**, 1320 (1934).

(20) A. Kailan, *Z. physik. Chem.*, **95**, 215 (1920).

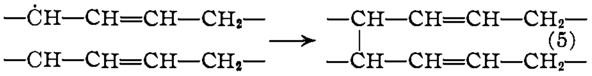
(21) R. L. Platzman, *Radiation Research*, **2**, 1 (1955).

of the corresponding *cis* –CD=CD– units originally present in this polymer. Moreover, the rate of isomerization in DCPB was roughly of the same order of magnitude as in ordinary CPB. The nearly complete absence of migration fits in well with the views on intramolecular energy transfer advanced above and indicates that such transfer for the most part occurs before the energy is consumed in breaking C–H bonds. As a result, very few free radical sites are formed alpha to the double bonds, and what crosslinking does occur in the solid CPB polymer probably takes place mainly through very fast ion-molecule (and perhaps also Stern-Volmer) processes



$$\begin{array}{l}-\overset{+}{C}H_2-CH{=}CH-CH_2- \\ -CH_2-CH{=}CH-CH_2-\end{array} \longrightarrow \begin{array}{l}-CH-CH{=}CH-CH_2- \\ \quad | \\ -CH-CH{=}CH-CH_2-\end{array} + H_2^+ \quad (4)$$

rather than through free radical combination processes



$$\begin{array}{l}-\dot{C}H-CH{=}CH-CH_2- \\ -CH-CH{=}CH-CH_2-\end{array} \longrightarrow \begin{array}{l}-CH-CH{=}CH-CH_2- \\ \quad | \\ -CH-CH{=}CH-CH_2-\end{array} \quad (5)$$

which can be expected to be infrequent. Weiss[22] has recently stressed the importance of a reaction such as (4) while tending to reject a reaction such as (5).

Apart from noting that free radicals probably do not play an important role in the γ-irradiation of solid polybutadiene, it is worth pointing out that no free radical has ever been found to promote the isomerization of this polymer other than the bromine or thiyl radical considered previously,[23] and these, of course, were not present in the system examined here. Thus, free radicals are not involved in the unsensitized isomerization of polybutadiene, which is instead an interesting example of a radiation induced reaction involving energy transfer processes exclusively.

The function of the antioxidant in inhibiting the solid state isomerization can best be accounted for in terms of quenching of excited states in the manner discussed over thirty years ago by Privault[2,3] and Perrin.[24]

To conclude, reference should be made to the very recent work of Williams and Dole[13] who found that in the γ-irradiation of polyethylene–polybutadiene blends at 142° the polybutadiene component underwent *cis–trans* isomerization. Although the *G*-value for this reaction was not determined by these workers, a rough estimate by the present author indicates a value of around 3 *cis* double bonds isomerized per 100 e.v. absorbed by the polymer blend. Since the blend contained 5% CPB, the yield based on the energy absorbed only by the latter polymer is about 60, or some 4 times the yield of the pure CPB polymer (14.6). It follows, therefore, that about three times as much energy was transferred intermolecularly from the polyethylene to the polybutadiene in the blend as was absorbed directly by the latter polymer. This transfer of energy which apparently "sensitizes" the CPB isomerization was also responsible for "protecting" polyethylene to some extent against vinyl decay and evolution of hydrogen. Further research on the energy yields in the isomerization of CPB in various blends with polyethylene would be of considerable theoretical interest.

Acknowledgments.—The author wishes to thank R. J. Minchak and H. Tucker for kindly furnishing the samples of CPB and TPB used in this work. The polybutadiene-2,3-d_2 was made available through the efforts of D. Craig, R. B. Fowler and H. Tucker. These stereospecific polymers were prepared on projects sponsored by Goodrich-Gulf Chemicals, Inc. Thanks are also due Jane Ferguson and J. J. Shipman for assistance with the infrared analyses.

---

[22] J. Weiss, *J. Polymer Sci.*, **29**, 425 (1958).

[23] M. Privault, *Compt. rend.*, **184**, 1120 (1927).

[24] F. Perrin, *ibid.*, **184**, 1121 (1927).