absorption due to change in concentration of TTA during reaction was so small that it was neglected. Equilibrium optical densities correspond to a steady state of at least twenty minutes duration in the case of complex formation with $\mathrm{Sc^{III}}$, $\mathrm{Cu^{II}}$, $\mathrm{Mg^{II}}$ and $\mathrm{Zn^{II}}$ and were generally obtained within six minutes. According to expectations for equilibrium in first-complex formation, the steady-state period was obtained after 8 to 10 half-lives of the initial rate. With $\mathrm{Fe^{III}}$, reaction was followed for about 20 minutes and a steady state was reached after 40 minutes. With $\mathrm{Al^{III}}$ the reaction was followed for 200 to 300 min. and a steady optical density was reached in about 1000 min. To prevent evaporation of solution during this long period of standing, shellac was used to seal the caps of the absorption cells.

Materials.—The TTA used (m.p. 44–45°) was obtained from the Dow Chemical Company. Solutions of TTA were obtained by dissolving a weighed amount of the solid in a known volume of water and preparing the desired concentrations by dilution of this standard solution. All stock solutions of metal salts were prepared in nitric acid solution to prevent hydrolysis. Iron(III) and scandium(III) nitrate solutions were standardized by precipitation of iron and scandium with NH_4OH and ignition of the precipitates to Fe_2O_3 and Sc_2O_3, respectively.[23,24] Stock solutions of the other metal ions were prepared from weighed amounts of high purity nitrate salts.

Acknowledgments.—The authors express their appreciation to Dr. W. C. Fernelius for his encouragement in the initiation and during the progress of the present study. We are indebted to Dr. R. G. Pearson for comments on the manuscript. The authors gratefully acknowledge financial support furnished for this work by the United States Atomic Energy Commission through Contract AT(30-1)-907.

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

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

BY MORTON A. GOLUB

RECEIVED JULY 18, 1958

The kinetics of the γ-ray induced *cis–trans* isomerization of polybutadiene in benzene were studied over the temperature range 20 to 60°, using diphenyl disulfide as a sensitizer. The isomerization is first order with respect to the *cis* content in the polymer, the rate varying with $[C_6H_5SSC_6H_5]^n$ where n ranges from somewhat greater than 1 at small concentrations of the sensitizer to less than $^1/_2$ at high concentrations. The number of double bonds changed from *cis* to *trans* configuration per 100 e.v. of energy absorbed by the combined polymer–solvent–sensitizer system can exceed 1000. Chain lengths of the order of 10^4 were observed. The mechanism is believed to involve geometric interconversion of the transitory isomeric radical adducts formed from the polymer double bonds and the thiyl radicals generated in the radiolysis of the sensitizer. The over-all activation energy for the radiation induced isomerization, sensitized by diphenyl disulfide, was found to be 2.3 ± 0.3 kcal./mole.

Introduction

The photochemical *cis–trans* isomerization of polybutadiene in solution sensitized by bromine atoms or thiyl radicals was described earlier[2] and considered to occur through a mechanism comparable to that depicted for the isomerization of simple olefins involving the same type of sensitizers.[3] Thus, it was assumed that addition of the bromine atom or thiyl radical to the double bond in the polymer molecule forms a transitory radical structure in which free rotation is possible about the carbon–carbon bond originally present as a double bond. When the attached atom or radical is subsequently released with re-establishment of the double bond, the configuration formed predominantly is the thermodynamically more stable one which, for polybutadiene, is evidently the *trans* form.

Recently, the analogous radiation induced isomerization of this polymer sensitized by bromine atoms was investigated[4] and found to be quite similar to the corresponding photochemical reaction.[2] The present work was undertaken to pursue further the analogy between the photochemical and radiation chemical processes and is concerned with reporting kinetic data for the thiyl radical sensitized γ-ray induced *cis–trans* isomerization of polybutadiene in benzene.

Although the aliphatic disulfides and mercaptans generally are rather weak sensitizers for the radiation chemical isomerization, compared to the organic bromides studied previously,[4] many of the aromatic disulfides, however, are very strong sensitizers. Diphenyl disulfide was selected for use in the present work because it is a very potent source of thiyl radicals and is readily available. It is so efficient in this respect that chain lengths of the order of 10^4 easily were obtained for the isomerization.

Experimental

The polybutadiene samples used in this work were prepared by stereospecific polymerization of 1,3-butadiene to a predominantly *cis* configuration. The viscosity average molecular weights ranged from about 100,000 to 350,000. The polymer structure, as determined by infrared analysis, consisted of approximately 95% *cis*-1,4- and 2% *trans*-1,4 units, with the remaining unsaturation made up of vinyl side groups resulting from 1,2-addition polymerization. Since the last-mentioned type of double bonds was not involved in the isomerization, only the per cent. *cis* double bonds, or *cis/trans* ratio, in the polymer before and after irradiation was important in this study. From an initial *cis/trans* ratio of 98/2, the polymer could be isomerized with diphenyl disulfide at room temperature to an equilibrium *cis/trans* ratio of about 8/92.

Stock solutions of the very high *cis* polybutadiene in benzene, with and without antioxidant, were prepared for γ-irradiation to a polymer concentration of about 10 g./l.

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(1) Presented at the Eighth Canadian High Polymer Forum at MacDonald College, Ste. Anne de Bellevue, Quebec, May, 1958. Work was accomplished under Air Force contract, the sponsoring agency being the Materials Laboratory of Wright Air Development Center.

(2) M. A. Golub, *J. Polymer Sci.*, **25**, 373 (1957).

(3) For the bromine case, see H. Steinmetz and R. M. Noyes, THIS JOURNAL, **74**, 4141 (1952); for the thiyl case, see R. Townshend, R. Pallen and C. Sivertz, Abstract, 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

(4) M. A. Golub, THIS JOURNAL, **80**, 1794 (1958).

The polymer as received contained the antioxidants N,N′-di-2-naphthyl-*p*-phenylenediamine and N,N′-diphenyl-*p*-phenylenediamine to the extent of about 1% and 0.5% by weight, respectively, based on polymer. The polybutadiene was dissolved in benzene, the resulting solution filtered to remove small amounts of insoluble material, diluted to the appropriate concentration and used as such for the antioxidant-containing solution. To a part of the original solution methanol was added, precipitating the polymer, which was then washed with further alcohol, air-dried and redissolved in benzene to give a solution of the purified polymer free of antioxidant.

Various amounts of diphenyl disulfide were added to portions of the stock solutions to provide the desired thiyl radicals on γ-irradiation. C.P. materials were used throughout. The sensitized solutions were placed in ordinary screw cap glass bottles (amber-colored to prevent any visible light induced isomerization during handling) and irradiated under nitrogen at several temperatures in the range of 20 to 60° for various periods of time in a 335 curie Co^{60} γ-ray source having a radiation flux of about 1.3×10^5 r./hr. Aliquots of the irradiated solutions were withdrawn after various doses, and the dissolved polymers precipitated with methanol and redissolved in benzene. The cleaned-up polymer samples were then analyzed for residual *cis* content by infrared absorption using a Perkin–Elmer Model 21 spectrophotometer. The spectra were run on thin polymer films cast on rock salt plates from the benzene solutions. The method of calculating the *cis*/*trans* ratio was described in the previous paper.[4] However, a newer value of 1.89 for the ratio of the extinction coefficient of the *trans* to that of the *cis* band was used in the present calculations, instead of the previous value of 1.63. In routine spectroscopic examination of the irradiated polymers, the infrared absorption was confined to the 9 to 15 micron range which contains the *trans* band at 10.35 μ and the *cis* band at 13.6 μ.

Typical infrared spectra from 2 to 15 μ for a high *cis*-polybutadiene before and after isomerization (sensitized by bromine atoms), as well as a high *trans*-polybutadiene polymerized directly, were shown previously.[4] It was not necessary to present here a typical spectrum of the polymer isomerized by means of thiyl radicals, since it was very similar to the spectra obtained in the bromine case. Apart from showing the *cis–trans* conversion, the spectra indicated that no other structural changes occurred in the polymer during irradiation with diphenyl disulfide. In particular, there was no evidence for any mercaptan addition to the polymer or any decrease in the unsaturation. Microanalysis for sulfur and chemical determination of unsaturation confirmed the view that the polymer structure was otherwise unaltered in the course of the isomerization.

Unlike the bromine sensitized case where γ-irradiation under nitrogen resulted in considerable gelation of the polymer, in the thiyl case only a very small amount of degradation generally occurred, so that the irradiated polymer remained soluble and could always be recovered and purified. This clean-up of polymer was essential in order to avoid trace amounts of the disulfide in the polymer film which would give rise to bands in the infrared spectrum which interfere with the *cis* band and make it impossible to determine the *cis*/*trans* ratio accurately. As in the previous work,[4] irradiations in air led to fairly rapid degradation, so that all the irradiation runs reported here were carried out under nitrogen. The rate of the isomerization sensitized by the thiyl radicals was completely unaffected by any change in molecular weight accompanying the irradiation in the absence of air. Oxygen, however, was seen to have a retarding effect on the isomerization which is consistent with the chain nature of the reaction.

Results

Typical kinetic plots for the γ-ray induced isomerization of polybutadiene in benzene in the presence of diphenyl disulfide at 24 to 26° are shown in Fig. 1. These plots correspond to the expression for a first-order reversible process

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

where K is the equilibrium constant for the *cis–trans* interconversion, x is the per cent. *cis* changed into *trans* for a radiation dose R, x_e is the per cent. *cis* converted at equilibrium and k is the pseudo first-order rate constant for the isomerization which depends on the sensitizer concentration. Since the *cis*/*trans* ratio initially was 98/2 and at equilibrium 8/92, K and x_e had the values 11.5 and 90%, respectively, for the isomerization runs at room temperature. Some departure from linearity in the kinetic plots occurs at the higher doses and is attributed to a slow, continuous decrease in the steady-state concentration of the thiyl radicals.

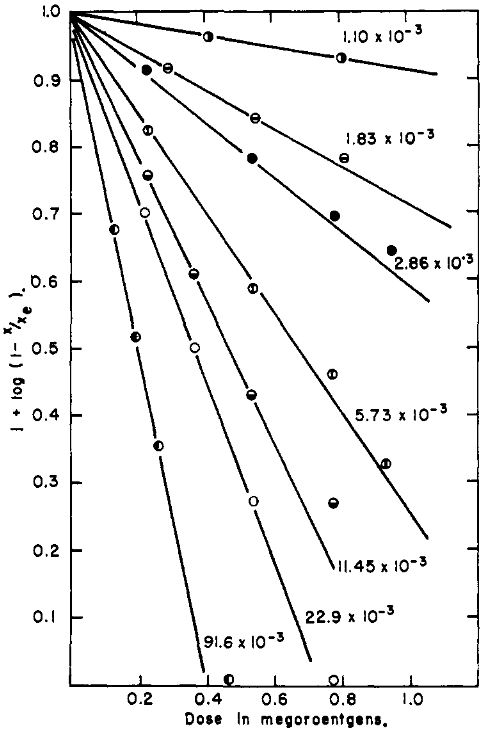

Fig. 1.—Kinetic plots for the thiyl radical sensitized isomerization of polybutadiene in benzene at 24 to 26°. Concentrations of diphenyl disulfide are given in mole/l.

Figure 2 shows a logarithmic plot of k against the concentration of diphenyl disulfide used in the various runs. The slope of this curve ranges from somewhat greater than 1 at small concentrations of the sensitizer to less than $^1/_2$ at high concentrations, which values represent the variation in the order of the reaction in diphenyl disulfide. The presence or absence of antioxidant was seen to have no effect on the rate of isomerization. Since the rate constant for the *unsensitized* isomerization in benzene,[4] *i.e.*, where no sensitizer was deliberately added to the polymer solution prior to γ-irradiation, was extremely small (3.8×10^{-9} r.$^{-1}$) compared to the isomerization rates obtained with the thiyl radicals, the values of k reported here were not corrected for the *unsensitized* reaction.

The kinetic data for the isomerizations carried out at room temperature are summarized in Table I. Since the value of the reaction yield G defined here as the number of *cis* double bonds isomerized per 100 e.v. of energy absorbed by the entire solution, falls off exponentially with dose, the value G_0 was determined for each run by extrapolating the G values to zero dose. These G_0 values are given in

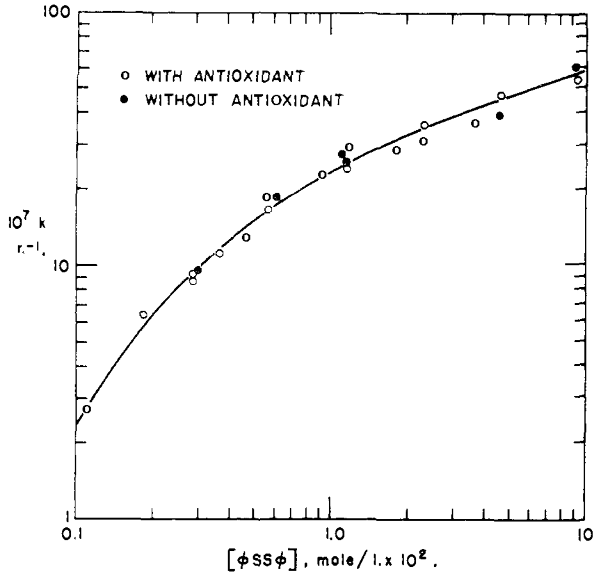

Fig. 2.—Dependence of the rate constant for the isomerization of polybutadiene at room temperature on the concentration of diphenyl disulfide.

the table. In calculating the reaction yields, it was assumed that both the polymer solution and the sensitizer absorbed 5.6 × 10^{19} e.v./g. per megaroentgen. The fourth column of Table I gives values for G_0^s, calculated as the number of *cis* double bonds isomerized per 100 e.v. absorbed directly by the sensitizer itself, assuming no energy transfer between the solvent or polymer and the sensitizer. This hypothetical quantity G_0^s would be analogous to the quantum yield in the corresponding photosensitized reaction where the optical energy absorbed in the system is completely taken up by the sensitizer.

TABLE I

RADIATION INDUCED ISOMERIZATION OF POLYBUTADIENE[a]

[$C_6H_5SSC_6H_5$], mole/l. × 10^2	10^7k, r.$^{-1}$	G_0[b]	$10^{-4}G_0^s$
9.160[c]	59.6	1320	6.00
9.160	53.0	1130	5.13
4.602[c]	38.6	955	8.58
4.580	45.6	1020	9.12
2.290	35.3	895	16.0
1.145	30.1	610	21.7
0.612[c]	18.8	510	34.1
.302[c]	9.67	282	38.0
.286	9.30	260	38.5
.110	2.70	58.0	21.5

[a] Temperature, 24–26°. [b] Not corrected for the *unsensitized* reaction for which G_0 was 0.92. [c] Without antioxidant. All other solutions contained antioxidant.

Now, energy transfer *does* occur and is of considerable importance in radiation chemistry. However, for a solution of diphenyl disulfide in benzene, it may not be unreasonable to assume, as a rough approximation, that the energy lost by the excited disulfide molecules in collisions of the second kind with benzene molecules is, within a factor of ten or so, comparable to the energy acquired by the unexcited sensitizer molecules in collisions with excited solvent molecules. If this is so, then, from the standpoint of energy utilization in the system under consideration, G_0^s may be a much better index of sensitizer efficiency than G_0. Certainly, in a very dilute solution of polybutadiene in benzene most of the excited solvent molecules ultimately lose their energy through collisions with other solvent molecules and hence transfer little energy to the solute. It is seen in Table I that, although the yield G_0 increased with increase in the concentration of the disulfide, the value of G_0^s steadily decreased with increase in concentration. This would be expected on the basis of a higher rate of recombination of the $C_6H_5S\cdot$ radicals to give $C_6H_5SSC_6H_5$ in the more concentrated solution of sensitizer, which would reduce the chain length of the reaction and thereby the calculated energy yield for the thiyl radicals.

Data for the effect of temperature on the rate of the thiyl radical sensitized isomerization are presented in Table II from which the Arrhenius plots of Fig. 3 were derived. The over-all activation energy for this reaction was calculated to be 2.3 ± 0.3 kcal./mole. For these calculations it was assumed that the equilibrium constant K had the value 11.5 at 24°, 10.5 at 38°, 9.6 at 50° and 9.0 at 60°. These data lead to an estimation of the following thermodynamic quantities for the equilibrium *cis–trans* interconversion of the internal double bonds in polybutadiene in benzene at 24°: $K = 11.5 \pm 0.3$, $\Delta F^0 = -1450 \pm 30$ cal./mole, $\Delta H^0 = -1350 \pm 350$ cal./mole and $\Delta S^0 = 0.3 \pm 1.3$ cal./mole deg.

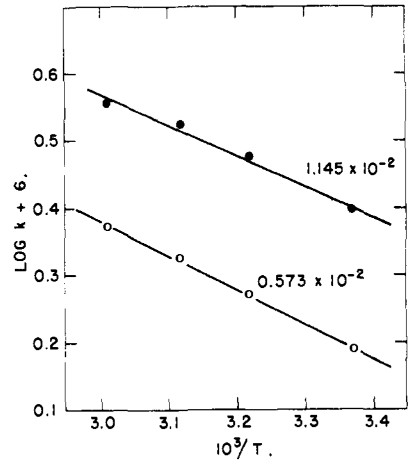

Fig. 3.—Arrhenius plots for the thiyl radical sensitized isomerization of polybutadiene. Concentrations of diphenyl disulfide are given in mole/l.

TABLE II

EFFECT OF TEMPERATURE ON THE RATE OF ISOMERIZATION

Temp., °C.	[$C_6H_5SSC_6H_5$], mole/l. × 10^2	10^7k, r.$^{-1}$
23.9 ± 1.0	1.145	25.0
	0.573	15.4
37.8 ± 1.0	1.145	29.7
	0.573	18.6
50.0 ± 1.0	1.145	33.5
	0.573	21.2
60.2 ± 1.0	1.145	36.0
	0.573	23.7

Discussion

The *cis–trans* isomerization of polybutadiene in solution on γ-irradiation in the presence of diphenyl disulfide is viewed as involving the formation of a composite radical structure from the polymer double bond, either *cis* or *trans*, and the $C_6H_5S\cdot$ radicals formed in the radiolysis of the disulfide. The transitory isomeric radicals thus formed can then interconvert.

$$C_6H_5S\cdot + cis \rightleftarrows C_6H_5S\text{-}cis\cdot \qquad (1)$$

$$C_6H_5S\cdot + trans \rightleftarrows C_6H_5S\text{-}trans\cdot \qquad (2)$$

$$C_6H_5S\text{-}cis\cdot \rightleftarrows C_6H_5S\text{-}trans\cdot \qquad (3)$$

On release of the attached thiyl radicals the double bonds are re-established with the *trans* configuration being formed predominantly.

The $C_6H_5S\cdot$ radicals can be produced in a variety of ways, as partially indicated by these possible reactions.

$$C_6H_6 \rightsquigarrow C_6H_6{}^* \qquad (4)$$

$$C_6H_6{}^* + C_6H_5SSC_6H_5 \longrightarrow C_6H_6 + C_6H_5SSC_6H_5{}^* \qquad (5)$$

$$C_6H_5SSC_6H_5{}^* \longrightarrow C_6H_5S\cdot + C_6H_5S\cdot \qquad (6)$$

$$C_6H_5SSC_6H_5 \rightsquigarrow C_6H_5S\cdot + C_6H_5S\cdot \qquad (7)$$

$$R\cdot + C_6H_5SSC_6H_5 \longrightarrow RSC_6H_5 + C_6H_5S\cdot \qquad (8)$$

$R\cdot$ can be a hydrogen atom or some radical formed from one of the components of the solution.

The $C_6H_5S\cdot$ radicals can also take part in the chain terminating reactions

$$C_6H_5S\cdot + C_6H_5S\cdot \longrightarrow C_6H_5SSC_6H_5 \qquad (9)$$

$$C_6H_5S\cdot + R\cdot \longrightarrow RSC_6H_5 \qquad (10)$$

$$C_6H_5S\cdot + H\text{--} \longrightarrow C_6H_5SH \qquad (11)$$

This last reaction symbolically represents any hydrogen abstraction by the thiyl radical, such as that involving the methylenic hydrogen atoms in the polymer chain. Both C_6H_5SH and RSC_6H_5, once formed, could subsequently dissociate on further excitation

$$C_6H_5SH \text{ (or } RSC_6H_5) \rightsquigarrow H \text{ (or } R\cdot) + C_6H_5S\cdot \qquad (12)$$

but their concentrations presumably build up slowly during the course of the irradiation runs. This has the effect of reducing the concentration of diphenyl disulfide in the system and hence also the steady-state concentration of the $C_6H_5S\cdot$ radicals. In a typical isomerization run with a polymer solution containing about 5 g./l. of $C_6H_5SSC_6H_5$ the amount of C_6H_5SH formed after a dose of about one megaroentgen was about 0.2 g./l.

Other processes doubtless occur on irradiation of the sensitized polymer solution, such as those leading to some chain scission in the polymer and those giving rise to an assortment of radiolytic products directly from bond rupture in the substances present in the irradiated system, as well as through interaction of the various fragments formed. However, these other processes are considered to be unimportant in the isomerization kinetics. No mercaptan addition to the polymer was observed in this work, although such a reaction could be initiated at much higher concentrations of polymer and diphenyl disulfide than were used in this study.

The recombination reaction 9 constitutes the reverse of the radiolysis of the disulfide (reactions 6 and 7). These together with processes 8, 10, 11 and 12 serve to establish a more or less steady state concentration of $C_6H_5S\cdot$ radicals. Actually, however, there is a slow, continual decrease in $[C_6H_5S\cdot]$ during the isomerization runs as indicated by the departure from linearity in the first order plots of Fig. 1 at the higher radiation doses. This is presumably due to the formation of products like C_6H_5SH and RSC_6H_5 which remove the $C_6H_5S\cdot$ radicals from the system faster than they are returned through further dissociation of these products. At high concentrations of diphenyl disulfide, reaction 9 should be the principal termination reaction for the thiyl radicals, so that the steady state $[C_6H_5S\cdot]$, and hence also the pseudo first-order rate constant for the isomerization, should be proportional to $[C_6H_5SSC_6H_5]^{1/2}$. At low concentrations of the disulfide, on the other hand, reactions 10 and 11 should be relatively much more important than reaction 9, since the probability of two $C_6H_5S\cdot$ radicals colliding and recombining is considerably smaller than the probability for removal of these radicals *via* hydrogen abstraction or interaction with other organic radicals in the system. Accordingly, it would be expected that, at low concentrations of the sensitizer, the steady-state $[C_6H_5S\cdot]$, and therefore also k, would be roughly proportional to $[C_6H_5SSC_6H_5]$. This accounts in a general way for the fact that the isomerization rate was found to depend upon $[C_6H_5SSC_6H_5]^n$ where n ranges from about 1 at low concentrations of the sensitizer to about $^1/_2$ at the high concentrations.

In determining the efficiency of a sensitizer in a radiation induced reaction in solution, there is always the problem of ascertaining the contribution to the over-all yield made by energy transfer between the various components. In the present instance, such information would be useful in arriving at the chain length for the isomerization sensitized by thiyl radicals. This would be the number of *cis* double bonds isomerized per $C_6H_5S\cdot$ radical at the start of the reaction, since the forward rate falls off with increasing number of *trans* bonds formed.

It was suggested earlier in this paper that $G_0{}^s$ may be a much better measure of the sensitizer efficiency than G_0. The assumption was made there that the excitational energy given up by the disulfide molecules was, within a factor of ten or so, comparable to that acquired by these molecules in collisions of the second kind with solvent molecules. The reasonableness of this assumption may be seen from a consideration of the recent work of Fontijn and Spinks.[5] They studied the radiation induced addition of *n*-butyl mercaptan to pentene-1 and obtained typical G values for this reaction of about 5×10^4 for molar solutions of these reagents in cyclohexane and about 1.5×10^4 in benzene. In the absence of solvent (solution 4.5 molar in mercaptan and 4.7 molar in pentene) they obtained G values of about 2×10^5. Thus, in the radiation chemistry of a mercaptan, which should be more or less comparable to that of the disulfide considered here, it was observed that benzene exerted a protective effect resulting in a reaction yield of about a third of that

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(5) A. Fontijn and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1384, 1397, 1410 (1957).

in cyclohexane and about a tenth of that in the absence of solvent. Thus, if anything, relatively more energy was transferred from the mercaptan molecules to the benzene molecules than the reverse. Furthermore, the values of G_0^s for the isomerization (varying from 6×10^4 to 3.8×10^5) are obviously very much closer to the above-mentioned G values for mercaptan addition to the olefin than are the G_0 values (from about 1300 to 250, respectively).

An estimate of the chain length of the thiyl radical sensitized isomerization of polybutadiene can now be made. From a consideration of the results of Fontijn and Spinks cited above, it may be concluded that G_0^s affords a reasonable measure of the number of *cis* double bonds isomerized per 100 e.v. absorbed directly and indirectly by the sensitizer. By analogy with the photolysis of diphenyl disulfide[6] using λ 2537, a quantum of around 5 e.v. in the radiation case can dissociate a molecule of $C_6H_5SSC_6H_5$ into $C_6H_5S\cdot$ radicals, so that about 40 such radicals can be produced per 100 e.v. absorbed by the disulfide. Because of cage effects and possible protection by benzene, it is likely that the number of radicals actually produced per 100 e.v. of energy absorbed by the disulfide will be much less than 40. At any rate, since a G_0^s value as high as 4×10^5 was obtained in this work, it would follow that the $C_6H_5S\cdot$ radical can isomerize at least about 10^4 double bonds before being removed by any of the termination reactions discussed above. The chain length for the isomerization involving thiyl radicals is therefore of the same order of magnitude as that for the photochemical[7] and radiation chemical[5] addition of *n*-butyl mercaptan to pentene-1.

Acknowledgments.—The author wishes to thank R. J. Minchak and N. Hsu for kindly furnishing the high *cis*-polybutadiene used in this work, and Jane Ferguson and others of the infrared group for providing the required spectra.

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BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolysis of Polymethylvinyl Ketone and Polymethyl Isopropenyl Ketone[1]

BY K. F. WISSBRUN[2]

RECEIVED JULY 10, 1958

Films of polymethyl vinyl ketone and of polymethyl isopropenyl ketone have been photolyzed. Polymethyl vinyl ketone undergoes free radical dissociation and the Norrish Type II reaction. Polymethyl isopropenyl ketone degrades quantitatively to monomer, with a complicated dependence on molecular weight, temperature and intensity.

Introduction

The recent increased interest in the mechanisms of polymer degradation has resulted in a better understanding of the processes involved. Much of the work has been summarized in the books by Jellinek[3] and Grassie.[4] The techniques of photochemistry have proved useful in studying the mechanisms of polymer degradation. In the present work these techniques have been applied to the photolysis of polymethyl vinyl ketone (PMVK) and of polymethyl isopropenyl ketone (PMIK). These polymers are suitable for such study because the photochemistry of ketones is comparatively well understood. Also, the role of the carbonyl group as an intermediate in the photoöxidation of polymers makes a better knowledge of its behavior in polymeric systems desirable.

During the course of this work the results of Guillet and Norrish[5] on the photolysis of dioxane solutions of PMVK were published. The present work, done on films of the polymer rather than on solutions, agrees with that of Guillet and Norrish.

Experimental

Materials.—Anhydrous methyl vinyl ketone, distilled at 190 mm. under nitrogen, was degassed in a vacuum line, and a 70-g. sample was distilled into a bulb containing 0.585 g. of recrystallized benzoyl peroxide. The distillate was frozen at −196°, the bulb was sealed and allowed to stand 16 hr. at room temperature. The resulting clear, colorless gel was dissolved in chloroform and precipitated with excess benzene six times. The yield of dried polymer was about 2 g.; the intrinsic viscosity in acetone at 25° was 1.13 dl./g., corresponding to a molecular weight of about 200,000 from the data of ref. 5.

Thin films of PMVK were prepared by casting from a filtered dilute chloroform solution on mercury. The films, plasticized by residual solvent, were too soft and adherent to be handled easily, and they were therefore cast in a rectangular glass frame. After evaporation of the bulk of the solvent the frame was placed in a heated vacuum desiccator until the film was sufficiently dry to cut into 12 mm. square samples for the photolyses. Two series, designated B and C, were photolyzed. In each series the film thickness, determined by weighing and by optical density, was uniform to better than 5%. Assuming a density of 1.12 for the polymer,[6] the thicknesses were calculated to be 15.9 and 47.3 μ, respectively.

Three samples of PMIK were used in this work. The first, designated as G, was kindly supplied by the Celanese Corporation of America and was stated to have been prepared in 70% conversion in cyclohexane solution with azobisisobutyronitrile catalyst. The polymer was purified by repeated precipitation from chloroform solution by methanol, and a film was then cast on mercury.

The other two samples, designated K and L, were prepared by a method similar to that used for PMVK. Polymer

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(2) Research Laboratory, Celanese Corporation of America, Summit, New Jersey. Postdoctoral Fellow 1955–1957 under a grant to the Department of Chemistry, University of Rochester, by the Doctors Camille and Henry Dreyfus Foundation, Inc.

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