

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY, EMERYVILLE, CALIFORNIA]

## Kinetics of the Photoisomerization of Polybutadiene

By G. R. SEELY

RECEIVED JUNE 2, 1962

The kinetics were determined for the photoisomerization of *cis*-polybutadiene by diphenyl disulfide in 365 m $\mu$  light, in toluene and other solvents at 25°. The quantum yield of the reaction is in the neighborhood of 100. The rate of isomerization is first order in light intensity, and this is interpreted to mean that effective termination is by hydrogen abstraction rather than by radical recombination. Polybutadiene supplies most of the hydrogen, but some comes from the solvent. The chain length is about 370 double bonds attacked for each phenylthiyl radical liberated. Evidence is advanced to support a primary quantum yield of about 0.13 for the dissociation of diphenyl disulfide under these conditions. The polymer does not degrade or crosslink during isomerization.

## Introduction

The isomerization of the double bonds of polybutadiene from the *cis* to the *trans* configuration by thiyl radicals or bromine atoms has been demonstrated recently by Golub.<sup>1,2,3</sup> The radicals may be formed by photolysis<sup>1</sup> or radiolysis<sup>2,3</sup> of bromides, mercaptans, or disulfides. Isomerization can also be induced thermally with sulfur<sup>4</sup> or selenium.<sup>5</sup> Equilibrium is reached when about 92% of the double bonds are in the *trans* configuration.<sup>3</sup>

Since isomerization proves a possible means of preparing a series of polymers having the same molecular weight and extent of branching, but differing in the ratio of *cis* and *trans* butene units, it became of interest to determine the quantum yield, and examine other aspects of the reaction which might affect its use. The present paper is concerned with the kinetics and mechanism of the isomerization of initially high-*cis* polybutadiene in solution at 25° by diphenyl disulfide and 365 m $\mu$  light. In addition to determining the rate and quantum yield, the extent of degradation, crosslinking, and sulfur incorporation were checked. The solvent usually was toluene, though benzene, heptane, and cyclohexene have been used for comparison.

## Experimental

Most of the runs were made with a locally prepared sample of polybutadiene composed of 95.7% *cis*, 1.6% *trans* and 2.7% 1,2-butene units. Its intrinsic viscosity in toluene at 25° was 2.88 dl./g.; its number-average and weight-average molecular weights were 125,000 and 420,000. The sample used for the remaining runs was 96.6% *cis*, 1.2% *trans*, 2.4% 1,2-butene, had an intrinsic viscosity of 2.1 dl./g. and a weight-average molecular weight of 320,000. The second sample gave essentially the same results as the first. The polymer was freed of antioxidant and other extractable impurities by two coagulations and dried in vacuum before use. The 1,2-butene content was unaffected by isomerization, and all results have been converted to a 1,2-butene-free basis.

Diphenyl disulfide was recrystallized three times from methanol. Solvents were all reagent grade and were used as received, except that cyclohexene was freed of peroxides.

Light shorter than 350 m $\mu$  was filtered from the output of a G.E. AH4 100-watt low pressure mercury lamp by a 2 cm. depth of a 1% solution of  $\beta$ -naphthol in toluene. Since light of 405 and 436 m $\mu$  is only slightly absorbed by diphenyl disulfide at the concentration (3 g./l.) usually employed, photolysis was brought about by essentially monochromatic 365 m $\mu$  light. Light absorbed in the reaction cell was measured by differential ferrioxalate actinometry, according to instructions given in the literature.<sup>6</sup> This method of

light measurement was particularly appropriate because of its sensitivity to the actinic 365 m $\mu$  light, compared with light of longer wave length.

Nitrogen was bubbled through the reaction and actinometer cells before and during isomerization. Separate experiments had shown that the presence of oxygen during photolysis led to rapid degradation of the polymer. Reaction, actinometer and filter cells were immersed in a circulating water-bath which held the temperature at 25  $\pm$  1°.

At the conclusion of the reaction the polymer was coagulated twice with 2-propanol and dried in vacuum. The *trans* content was calculated from the absorptivity of the peak at 10.34  $\mu$  in the infrared spectrum of solutions in carbon disulfide. The extinction coefficient of the *trans* peak, 2.63 l./g. cm., was determined from spectra of locally prepared samples of high-*trans* polybutadiene, and is a little higher than 2.54 l./g. cm. found by Hampton<sup>7</sup> and 2.46 l./g. cm. found by Silas, Yates, and Thornton.<sup>8</sup> The extinction coefficient of *cis*-polybutadiene at the same wave length was 0.082 l./g. cm.

Progress of the isomerization is expressed through an adjusted and normalized *cis* concentration

$$[cis]^* = \frac{[trans]_{eq} - [trans]}{[trans]_{eq} - [trans]_0} \quad (1)$$

which decreases from 1 at the start of reaction ( $[trans] = [trans]_0 = 0.016 [B]$ ) to 0 at equilibrium, when  $[trans]_{eq} = 0.95 [B]$ , where  $[B]$  is the total concentration of butene units, *cis* and *trans*. Here Golub's earlier estimate of the equilibrium *trans* concentration has been used.<sup>1</sup> If the later and better value<sup>8</sup> had been used,  $[trans]_{eq} = 0.92[B]$ , the results would have been affected only slightly in all cases but one in which an 86.5% *trans* content was attained.

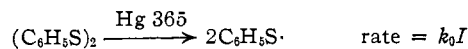
The supernatant left after the first coagulation of the polymer sometimes was analyzed for mercaptan by iodine titration. It was recognized tardily that without added base<sup>9</sup> the end-point color developed prematurely, and titers were low by a factor of about 2. Later titrations with a base (2,6-lutidine) present were accurate and had sharp end-points.

The polymer recovered after two coagulations was also sometimes analyzed for sulfur by a combustion method.

The intrinsic viscosity of the polymer was determined before and immediately after the reaction. A decrease was regarded as evidence of predominant degradation during the reaction, and an increase as evidence of predominant crosslinking. At no time was gel observed to form during the reactions.

## Results

The simplest mechanism conceivable for the isomerization consists of photolytic initiation



where  $I$  is the rate of light absorption, addition of radicals to the double bond of a butene unit ( $B$ ) in the polymer

(1) M. A. Golub, *J. Polymer Sci.*, **25**, 373 (1957).(2) M. A. Golub, *J. Am. Chem. Soc.*, **80**, 1794 (1958).(3) M. A. Golub, *ibid.*, **81**, 54 (1959).(4) W. A. Bishop, *J. Polymer Sci.*, **55**, 827 (1961).(5) M. A. Golub, *ibid.*, **36**, 523 (1959).(6) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956).(7) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).(8) R. S. Silas, J. Yates and V. Thornton, *ibid.*, **31**, 529 (1959).(9) D. P. Harnish and D. S. Tarbell, *ibid.*, **21**, 968 (1949).

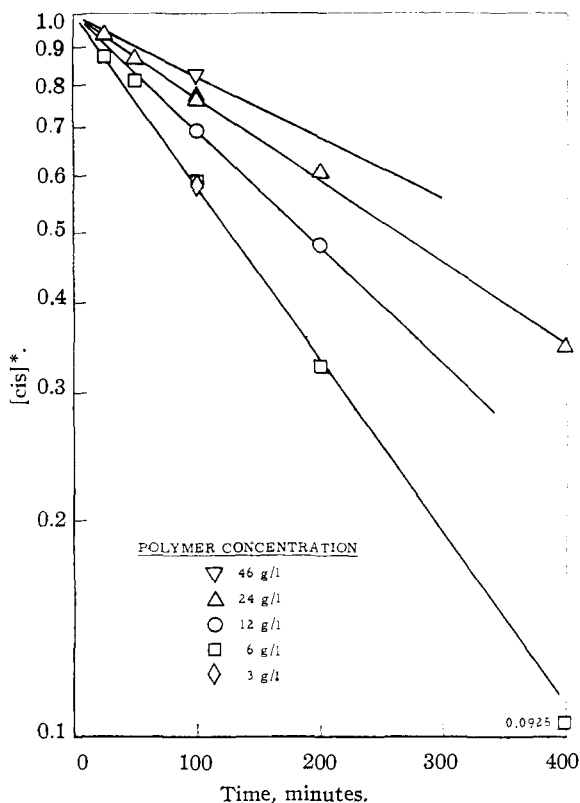
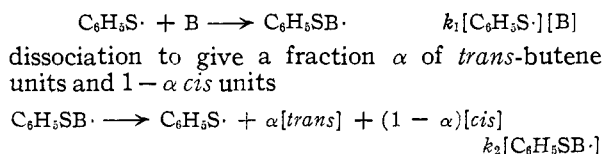


Fig. 1.—Dependence of the conversion of *cis* to *trans* on time and polymer concentration, at an approximately constant light absorption rate of  $1.2 \times 10^{-6}$  einsteins/l. min.;  $[cis]^*$  defined by (1) of text; diphenyl disulfide concentration 3 g./l.



and, finally, termination by recombination of radicals



This mechanism predicts that the conversion of *cis* to *trans* would be first order, and that the rate constant would depend on the square root of light intensity, but not on the polymer concentration. The results to be presented bear out the first prediction but not the latter two.

The effect of varying concentration and time on the extent of isomerization is shown in Fig. 1. The data, plotted semilogarithmically, fall on straight lines, one for each concentration, which permit definition of the first order rate constant  $k$

$$[cis]^* = \exp(-kt) \quad (2)$$

The value of  $k$  decreases as polymer concentration increases, yet not so rapidly as to be reciprocal to the concentration.

Although the per cent. isomerization rate, represented by  $[cis]^*$ , falls off with increasing concentration, it should be noted that the absolute isomerization rate, in moles/l./min., increases somewhat with concentration,

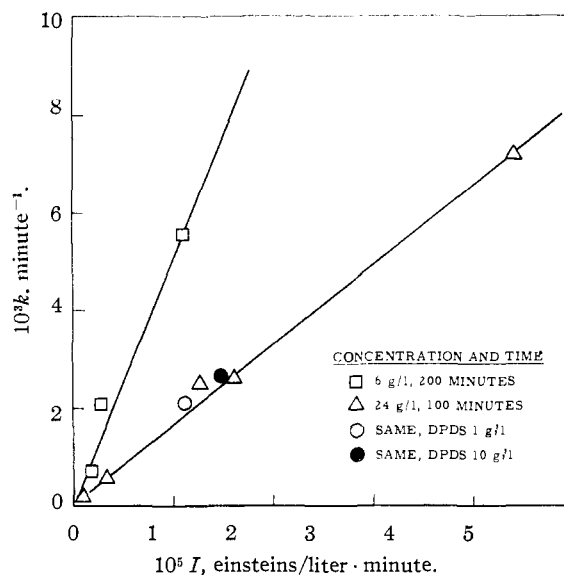


Fig. 2.—Dependence of first order rate constant for isomerization on light intensity, at fixed concentrations and times: diphenyl disulfide (DPDS) concentrations, 3 g./l. except as noted.

The effect of varying the light intensity on  $k$  is shown in Fig. 2, at two concentrations and reaction times. The data, particularly at 24 g./l. polymer, show quite clearly that  $k$  is proportional to the first power of light intensity and not to the square root. We may therefore set

$$k = k'I \quad (3)$$

where  $k'$  still depends on the polymer concentration.

To see whether the disulfide concentration had any effect on  $k'$ , runs were made with 1 and 10 g./l. diphenyl disulfide in addition to those with the usual 3 g./l. The results, for 100 minute reactions at 24 g./l. polymer, showed no effect within experimental error. Points for these runs have been included in Fig. 2.

During isomerization the intrinsic viscosity of the polymer decreased by a variable amount averaging around 10%. The decrease is uncorrelated with the extent of isomerization, tends to be larger with smaller polymer concentrations, and is therefore attributed to degradation by residual oxygen. Significant intrinsic viscosity increases, 10 and 22%, were noted only when the solvent was heptane. It was concluded that isomerization is normally unaccompanied by significant degradation or crosslinking. The absence of gel at any time makes it highly unlikely that degradation and crosslinking proceeded at such rates as to cancel each other.<sup>10</sup>

#### Discussion

The discovery that  $k$  was directly proportional to light intensity was at first rather unexpected and could only have meant that termination took place not by recombination of phenylthiyl radicals but by some reaction involving only one radical. The presence of a characteristic odor after isomerization and the well documented ability of thiyl radicals to abstract hydrogen from

(10) R. W. Kilb, *J. Phys. Chem.*, **63**, 1838 (1959).

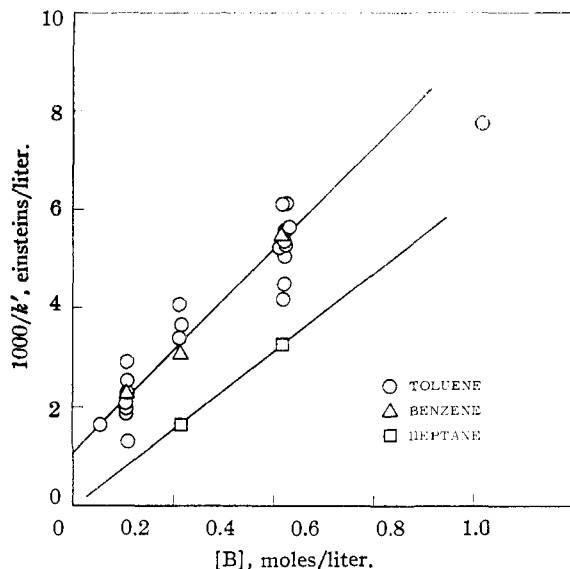


Fig. 3.—Plot of  $1/k'$  against  $[B]$  for runs in toluene, benzene, and heptane: test of equation (8).

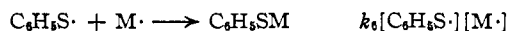
hydrocarbons<sup>11,12</sup> suggested that this reaction involved the formation of thiophenol. The decrease of  $k$  or  $k'$  with increasing polymer concentration implied that the polymer was supplying most of the abstractable hydrogen; lack of strict inverse proportionality to polymer concentration, however, suggested that the solvent (toluene) was also contributing hydrogen. From the better titrations, the amount of thiophenol formed during isomerization was  $13.5 \pm 1\%$  of the amount of light absorbed, assuming it to be the only reducing agent titrated.

Though the determination of sulfur incorporated into the polymer taxed the sensitivity of the analytical method, on the basis of twelve determinations on toluene runs the number of gram-atoms was found to be  $12.6 \pm 1\%$  of the number of einsteins of light absorbed. Thiophenol formation and sulfur incorporation are therefore about equally important in terminating isomerization chains.

One possible termination sequence to replace that of the previous reaction scheme starts with abstraction of hydrogen from polymer or solvent, forming thiophenol.



where  $\text{B}(\text{H})$  indicates the  $\text{B}$  contains an allylic hydrogen, and  $\text{MH}$  is the solvent. The most probable fate of the radicals  $\text{B}\cdot$  and  $\text{M}\cdot$  is to combine with a second thiyl radical. In this way sulfur becomes incorporated into the polymer.



If the usual steady state assumptions are made for the radical concentrations, the rate constants are now found to be

(11) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1137 (1959).

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 322ff.

$$k = \frac{k_0 k_1 I}{k_3 [\text{B}] + k_4 [\text{MH}]} \quad (4)$$

and

$$k' = \frac{k_0 k_1}{k_3 [\text{B}] + k_4 [\text{MH}]} \quad (5)$$

The quantum yield will be defined as the rate of addition of  $\text{C}_6\text{H}_5\text{S}\cdot$  to  $\text{B}$ , divided by the rate of light absorption.

$$\Phi = k_1 [\text{C}_6\text{H}_5\text{S}\cdot][\text{B}]/I \quad (6)$$

Since  $[\text{C}_6\text{H}_5\text{S}\cdot] = k_0 I / (k_3 [\text{B}] + k_4 [\text{MH}]) = k' I / k_1$  at steady state

$$\Phi = k' [\text{B}] \quad (7)$$

A referee has pointed out that there is an alternative termination sequence which will give similar kinetic expressions. In it,  $\text{C}_6\text{H}_5\text{SB}\cdot$  becomes inactivated by internal rearrangement or by reaction with another polymer or solvent molecule. A convenient internal rearrangement would be abstraction of hydrogen from a  $\text{CH}_2$  group three or more carbons away on the polymer chain, to form an allylic radical remote from the sulfur. In this sequence sulfur is first incorporated; in order to account for thiophenol formation, the allylic radical may disproportionate rather than combine with phenylthiyl. Such reactions are strongly suspected for sulfur radicals, especially bulky ones.<sup>11</sup>

Again it is possible that independent addition and abstraction reactions proceed at so similar a pace that the rates of sulfur incorporation and thiophenol formation are nearly equal. In view of these alternatives it is not possible to define the termination sequence more closely than to say that hydrogen abstraction and sulfur fixation are involved and that the solvent sometimes competes with polymer to provide hydrogen, as described below.

The kinetics of the reaction are in any case quite analogous to those found by Bartlett and Altschul for polymerization of allyl acetate,<sup>13</sup> except that here there is interference by the solvent in the termination.

**Effect of Solvent.**—If termination is by hydrogen abstraction, the choice of solvent for the reaction should be critical. That is, the rate of isomerization should be adversely affected by the presence of readily abstractable hydrogen in the solvent, which in turn should depend on the strength of the weakest C-H bonds of the solvent. On this basis, benzene (C-H bond energy 102 kcal./mole)<sup>14</sup> and heptane (about 96) should be relatively inert, toluene (77.5) and olefins (about 77) relatively active as hydrogen donors in competition with polymer.

A few runs were made in benzene, heptane and cyclohexene for comparison with toluene. The effect of solvent is best shown by plotting  $1/k'$  against  $[B]$  (Fig. 3). The intercept should be a measure of the reactivity of the solvent.

$$1/k' = (k_2/k_0 k_1)[\text{B}] + (k_4/k_0 k_1)[\text{MH}] \quad (8)$$

Heptane is inert as expected; termination is directly proportional to polymer concentration,

(13) P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, **67**, 816 (1945).

(14) Ref. 12, p. 50.

and approaches zero with [B]. In cyclohexene, isomerization proceeds only about 3% as fast as in toluene, also in line with expectations.

But in benzene isomerization unexpectedly occurred at exactly the same rate as in toluene. This is inexplicable in terms of C-H bond energies, and suggests that termination in aromatic solvents is more complicated than has been presented here. Addition of thiyl radicals to aromatic systems has been reported<sup>15</sup> and may be involved, but further experimentation is necessary before any conclusions can be reached.

From the slope and intercept of the benzene-toluene line in Fig. 3

$$k_3/k_0k_1 = 1.03 \times 10^{-3}$$

$$k_4[\text{MH}]/k_0k_1 = 1.05 \times 10^{-3} \text{ mole/liter}$$

Insertion of these values into the expression for quantum yield gives

$$\Phi = \frac{97}{1 + 0.102/[\text{B}]} \quad (9)$$

for isomerization in toluene and benzene.

**Initiation.**—Whatever the precise mechanism, the primary quantum yield of diphenyl disulfide photolysis is approximately equal to the quantum efficiency of thiophenol formation or sulfur incorporation, about 13%. It is possible to show theoretically that a primary quantum yield of this magnitude is to be expected.

Noyes, examining the effect of viscosity on the photodissociation of iodine, has derived and tested with good results expression (10) for the probability  $\phi$  of effective dissociation of an excited molecule into a pair of radicals.<sup>16</sup>

$$\frac{1}{1 - \phi} = \left(1 + \frac{m^{1/2}(h\nu - \epsilon)^{1/2}}{6\pi\eta a^2}\right) \left(1 + \frac{(3mkT/2)^{1/2}}{6\pi\eta a^2}\right) \quad (10)$$

- $m$  = mass of radical
- $a$  = radius of radical (as though spherical)
- $\eta$  = viscosity
- $\nu$  = frequency of exciting light
- $\epsilon$  = energy of bond broken
- $k$  = Boltzmann's constant

Phenylthiyl radical is not spherical, but a working value of its radius is obtained from the approximation  $3m/4\pi a^3 = \rho$ , where the density  $\rho$  is taken to be the same as that of chlorobenzene, 1.107 g./cm.<sup>3</sup>.

The proper value of the viscosity is not that of the solution, which depends on long range correlation of motion, but that of the solvent toluene, 0.5516 centipoise, which better represents the immediate neighborhood of the dissociating molecule.

The energy of the S-S bond has been much disputed in the past. A recent estimate,<sup>17</sup> and also one of the lowest, based on a revised heat of atomization of sulfur, is 54 kcal./mole. At the other extreme is the estimate of Franklin and Lumpkin,<sup>18</sup> 70 kcal./mole for aliphatic disulfides, based on electron impact studies. Though this value is

most probably too high for the bond energy, it may be more appropriate for the present calculation, because its use tacitly compensates for the fact that not all the excess energy is necessarily available to break the S-S bond. Light of 365 m $\mu$  supplies energy of 78.4 kcal./mole, leaving excess energies of 24.4 or 8.4 kcal./mole, depending on whether the low or high bond energy estimate is chosen.

On inserting these numbers into (10) the primary quantum yield becomes 0.152 or 0.102, bracketting the "observed" value 0.13. It is therefore not necessary to look further to find an explanation for the rate of effective photolysis of diphenyl disulfide.

Insertion of the value of  $k_0$  into that of  $k_3/k_0k_1$  gives  $k_3/k_1 = 1.34 \times 10^{-3}$ . The reciprocal of this, 750, is the ratio of isomerization to primary termination events. Since two radicals are formed in initiation, each radical accomplishes about 370 isomerizations, rather less than the chain length estimated by Golub.<sup>3</sup>

The fact that the viscosity of heptane is only about 2/3 that of toluene readily explains why the quantum yield in heptane is about 35% greater than the maximum possible yield in toluene according to (9).

Investigation of the quantum yield with 254 m $\mu$  light was precluded by the use of Pyrex vessels. However, one run was made without naphthol in the filter, which allowed light down to 300 m $\mu$  to enter the reaction cell. The light intensity was about 20% greater than in comparable runs with naphthol present, and the quantum yield was 10% greater than the median for other runs at that concentration. The increase is probably significant and is consistent with the above argument concerning the primary quantum yield.

The sign and magnitude of the activation energy were determined from 100 minute runs in toluene with 12 g./l. polymer at 5, 15, 25, 35 and 45°. Over this temperature range the activation energy was constant and equal to 3.67 kcal./mole, and about half of this, 1.95 kcal., can be accounted for by the effect of decreased viscosity on  $k_0$ .

In retrospect, it is easy to understand why hydrogen abstraction rather than radical recombination is the dominant termination reaction. Addition of phenylthiyl to an olefin is somewhat exothermic,<sup>12,19</sup> so that at any reasonable polymer concentration the predominant radical species will be that designated by C<sub>6</sub>H<sub>5</sub>SB·. Since this is attached to the polymer, it can diffuse only slowly, and so rarely encounters another radical. Effective travel of radicals occurs by dissociation of C<sub>6</sub>H<sub>5</sub>SB·, and migration of C<sub>6</sub>H<sub>5</sub>S· until it encounters another double bond. The quantum yield of isomerization then depends only on the relative probabilities of addition and hydrogen abstraction by C<sub>6</sub>H<sub>5</sub>S·, or of dissociation and rearrangement of C<sub>6</sub>H<sub>5</sub>SB·.

**Acknowledgments.**—The author is indebted to his colleagues for samples of polybutadiene and to Mr. J. V. Kaufman for assistance with the experimental work.

- (15) Y. Schaafsma, *Tetrahedron*, **10**, 76 (1960).
- (16) R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).
- (17) E. G. Lovering and K. J. Laidler, *Can. J. Chem.*, **38**, 2367 (1960).
- (18) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

- (19) C. Walling and W. Helmreich, *ibid.*, **81**, 1144 (1959).