

A Study on the Thermal Degradation of Rubber in Dilute Solutions*

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Introduction

The phenomenon of deterioration of rubber by aging is a complex process involving such diverse factors as effect of heat, light, oxidation, and hydrolysis, operating simultaneously. A study utilizing each factor separately may help to understand the mechanism of aging. Heat being one of the important causes of degradation we have been prompted to study the thermal degradation behavior of purified rubber.

Most of the earlier studies have been made with the bulk phase at high temperature (above 160°C.). Under these severe conditions there results complex compositions containing monomers, dimers, and other fragments which are difficult to identify.¹⁻³ Besides, in the bulk phase poor heat conductivity of the medium and slow rates of diffusion of the reactants and products of the reaction lead to complications and erroneous conclusions.

If the experiments are carried out under such conditions as low temperature in dilute solutions, most of the above-mentioned difficulties can be minimized. Such studies have an added advantage in that the cross-linking reaction, which sometimes accompanies the chain scission process and is appreciable during reaction in the bulk phase, would be minimized, at least in the early stages of degradation, since it is bimolecular. However, only a few viscometric⁴⁻⁶ studies of the low-temperature thermal degradation in solution have been made with GR-S rubber, deproteinized coagula, and crêpe rubber. Sometimes the solvents used were not inert; further, even though the viscometric technique is simple, it is not an absolute method of molecular weight determination. Moreover, the interpretation of the viscosity results may be complicated owing to uncertain factors such as the change in the shape of the molecule by degradation or otherwise.

The application of the light-scattering technique has several obvious advantages. We present a study made with this technique on the kinetics of thermal degradation of purified petroleum ether soluble, sol rubber in two inert solvents, viz. cyclohexane and *trans*-decalin, in the temperature range 60-100°C. Changes in molecular weight M_w , end-to-end distance

* Communication No. 529 from the National Chemical Laboratory, Poona-8, India.

$(\bar{r}^2)^{1/2}$, and solvent-solute interaction parameter A_2 have been evaluated at various stages of degradation.

Experimental

Rubber Purification

Deproteinized and deresinified petroleum ether soluble rubber was prepared from Hevae latex by the method of Pahl and Pummerer,⁷ and Noble.⁸

Degradation

The solvents cyclohexane and *trans*-decalin, were purified by standard methods. These were surface-distilled before the preparation of solutions for light-scattering experiments. A rubber solution of 40 ml. of 0.3 g./1000 ml. in cyclohexane was sealed in a Pyrex glass tube and kept at a certain temperature for a definite period of time. A thermostatted oven maintaining temperatures within $\pm 0.5^\circ\text{C}$. was used for this purpose. A separate sample from the same stock solution was used for each degradation experiment. The series of experiments was done at temperature intervals of 5°C . in the range of 60 – 100°C . No special precaution was taken to eliminate any photolytic reaction by excluding light from the experiments. At the end of each interval of time the tube was cooled to room temperature and the solution was filtered and used for light-scattering experiments.

Calibration of the Light-Scattering Photometer

Light-scattering studies were made with a B. S. light-scattering photometer supplied by the Phoenix Precision Instrument Co., Philadelphia, Pa. In all the experiments a cylindrical cell was used, the frosted semi-circular part had been blackened. A 4-mm. slit was used. Apart from the usual calibration of the neutral filters and working standard, the photometer was calibrated by means of a Styron sample supplied by Professor Debye. Assuming that the turbidity τ for a solution of polystyrene of 1.5 g./100 ml. is $3.5 \times 10^{-3} \text{ cm.}^{-1}$, correction factor of 1.2 was applied in the calculations of molecular weight, to account for changes in geometry due to changes in slit width and the changes from square cell to cylindrical cell.

The plots of HC/τ versus C have been employed to estimate M_w as a function of time. Here H is a constant for any particular solvent-solute system and equals $32\pi^3/3N\lambda^4 \mu_0^2 (d\mu/dC)^2$. (All the symbols have their usual significance.) The values obtained by extrapolation to zero concentration were corrected by the particle scattering factor $P(\theta)$ obtained from the dissymmetry data. The second virial coefficient A_2 (elsewhere denoted as solvent-solute interaction parameter) and the end-to-end

distance $(\bar{r}^2)^{1/2}$ assuming polydisperse coil have also been determined from the slope and the dissymmetry data, respectively.

Results and Discussion

Preliminary studies on degradation in the range of temperature 70–90°C. showed that the molecular weight decreases continuously with time and a point of inflexion is reached after which the molecular weight starts increasing (Fig. 1). In fact, after a sufficiently long interval of time visible opalescence occurs, probably due to crosslinking and microgel formation by the fragments of the rubber molecules. It may be seen that,

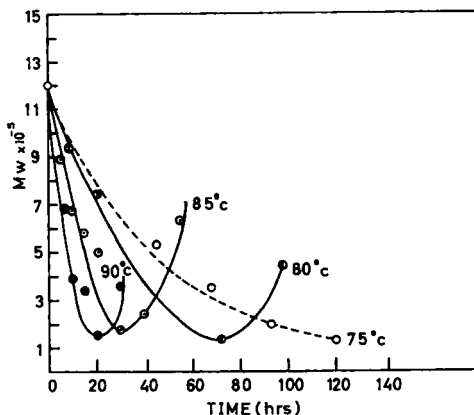


Fig. 1. Variation of M_w with time for rubber in cyclohexane.

as the temperature of degradation increases, the indication of the formation of crosslinked product appears at shorter time intervals. The appropriate periods of degradation were chosen on the basis of the above information so that the reaction is predominantly chain scission with negligible crosslinking.

Light-Scattering Data

The refractive index increments with concentration as determined by means of the Gladstone-Dale equation, and values of H , are given in Table I.

The molecular weight of a sample of rubber dissolved in cyclohexane decreased from 10.58×10^5 to 2.06×10^5 on degradation in the given range of temperature. This decrease occurred after 120 hr. at the lower temperature. For studies in decalin a sample from a different batch preparation was used. Here the molecular weight decreased from 11.44×10^5 to 5.84×10^5 in the temperature range of 80–95.7°C. when the sample was treated for periods of up to 15 hr.

The $(\bar{r}^2)^{1/2}$ changed from 2110 to 1170 Å. in the cyclohexane system and from 1540 to 1030 Å. in *trans*-decalin.

For the purpose of checking that the same type of linear products only are predominantly formed during the period of degradation studies, $(\bar{r}^2)^{1/2}/M_w$ values in the two solvents at various stages were determined (Tables II and III). In cyclohexane and *trans*-decalin they were 4.68 and

TABLE I*
Refractive Index Increment and H Values for Rubber in the Solutions

| Solvent | μ | $d\mu/dc$ | H |
|-----------------------|--------|-----------|------------------------|
| Cyclohexane | 1.4338 | 0.1238 | 4.790×10^{-6} |
| <i>trans</i> -Decalin | 1.4850 | 0.0684 | 1.550×10^{-6} |

* $\lambda = 4360$ A. at 25°C .

TABLE II
Rubber-Cyclohexane Series

| t , hr. | $M_w \times 10^{-5}$ | $(\bar{r}^2)^{1/2}$ | $(\bar{r}^2)/M_w$ |
|-------------------------|----------------------|---------------------|-------------------|
| At 70°C . | | | |
| 0.0 | 10.58 | 2110 | 4.21 |
| 5.0 | 9.95 | 2130 | 4.56 |
| 15.0 | 8.96 | 1820 | 3.69 |
| 48.0 | 6.07 | 1740 | 4.99 |
| 72.0 | 5.18 | 1600 | 4.94 |
| 96.0 | 4.77 | 1530 | 4.91 |
| 120.0 | 4.25 | 1430 | 4.81 |
| At 80°C . | | | |
| 0.0 | 10.58 | 2110 | 4.21 |
| 5.0 | 8.44 | 2150 | 5.48 |
| 9.0 | 7.40 | 1680 | 3.81 |
| 15.25 | 6.37 | 1670 | 4.38 |
| 21.50 | 5.81 | 1710 | 5.03 |
| 25.13 | 5.58 | 1650 | 4.88 |
| 33.00 | 4.80 | 1490 | 4.62 |
| 48.00 | 2.66 | 1170 | 6.15 |
| At 85°C . | | | |
| 0.0 | 10.58 | 2110 | 4.21 |
| 2.50 | 9.21 | 2090 | 4.74 |
| 5.00 | 7.95 | 1840 | 4.26 |
| 10.00 | 6.15 | 1690 | 4.65 |
| 12.90 | 6.04 | 1760 | 5.13 |
| 15.00 | 5.52 | 1720 | 5.36 |
| 21.00 | 4.56 | 1400 | 4.30 |
| At 90°C . | | | |
| 0.0 | 10.58 | 2110 | 4.21 |
| 5.0 | 6.38 | 1620 | 4.11 |
| 7.33 | 5.48 | 1540 | 4.33 |
| 10.00 | 4.41 | 1340 | 4.07 |
| 12.50 | 3.80 | 1450 | 5.53 |
| 15.00 | 3.26 | 1180 | 4.27 |

TABLE III
 Rubber-*trans*-Decalin Series

| <i>t</i> , hr. | $M_w \times 10^{-6}$ | $(\bar{r}^2)^{1/2}$ | $(\bar{r}^2)/M_w$ |
|----------------|----------------------|---------------------|-------------------|
| At 80°C. | | | |
| 0.00 | 11.44 | 1540 | 2.07 |
| 4.50 | 10.72 | 1600 | 2.39 |
| 7.00 | 10.44 | 1370 | 1.80 |
| 10.75 | 8.28 | 1250 | 1.89 |
| 12.00 | 8.48 | 1360 | 2.18 |
| 15.25 | 7.12 | 1210 | 2.06 |
| At 85.2°C. | | | |
| 0.00 | 11.44 | 1540 | 2.07 |
| 3.00 | 10.21 | 1410 | 1.95 |
| 5.00 | 9.47 | 1410 | 2.10 |
| 6.00 | 9.35 | 1530 | 2.50 |
| 7.00 | 8.67 | 1200 | 1.72 |
| 8.00 | 7.89 | 1200 | 1.82 |
| 9.00 | 7.74 | 1180 | 1.80 |
| 12.00 | 6.98 | 1260 | 2.27 |
| 14.11 | 6.53 | 1150 | 2.02 |
| At 90°C. | | | |
| 0.0 | 11.44 | 1540 | 2.07 |
| 5.00 | 8.54 | 1000 | 1.17 |
| 6.00 | 8.51 | 1340 | 2.11 |
| 7.00 | 7.27 | 1130 | 1.76 |
| 9.00 | 8.30 | 1450 | 2.53 |
| 13.00 | 6.90 | 1260 | 2.30 |
| 15.00 | 7.01 | 1180 | 1.99 |
| At 95.7°C. | | | |
| 0.0 | 11.44 | 1540 | 2.07 |
| 2.00 | 9.34 | 1430 | 2.19 |
| 4.00 | 7.79 | 1260 | 2.04 |
| 5.05 | 6.80 | 1190 | 2.08 |
| 6.00 | 6.62 | 1180 | 2.10 |
| 7.00 | 5.99 | 1090 | 1.98 |
| 9.00 | 5.84 | 1030 | 1.82 |

2.03 with a standard deviation of 0.48 and 0.27, respectively. The nearly constant $(\bar{r}^2)/M_w$ value obtained in each of the solvents shows that during the course of degradation branching was negligible.

Altgelt and Schulz,⁹ from their study of crêpe rubber in cyclohexane, reported for a sample of molecular weight 1.85×10^6 a radius of gyration of 1000 Å, i.e., an end-to-end distance of 2200 Å. This value is somewhat lower than our values of $(\bar{r}^2)^{1/2}$ for rubber of much lower molecular weight when a random walk model is assumed. This can be explained on the basis of the difference in the nature of the samples. The crêpe rubber contains a sizable proportion of gel rubber with a consequent shortening

of $(\bar{\tau}^2)^{1/2}$. This is borne out by the value 2.62 for $(\bar{\tau}^2)/M_w$ in the rubber-cyclohexane system calculated for Schulz's results, as compared with our value of 4.68.

The solvent-solute interaction parameter A_2 of the system rubber-cyclohexane before degradation is $1.34 \times 10^{-3} \text{ cm}^3\text{-g.}^{-2}\text{-mole}$, and of the rubber-decalin system it is $1.01 \times 10^{-3} \text{ cm}^3\text{-g.}^{-2}\text{-mole}$. The A_2 values of each system change owing to degradation, although the order of magnitude remains the same (in cyclohexane the minimum and the maximum values of A_2 are 0.82×10^{-3} and $3.60 \times 10^{-3} \text{ cm}^3\text{-g.}^{-2}\text{-mole}$, respectively, while in *trans*-decalin the corresponding values are 3.80×10^{-4} and $1.15 \times 10^{-3} \text{ cm}^3\text{-g.}^{-2}\text{-mole}$, respectively). This is to be expected, since polydispersity changes with degradation and is known to influence A_2 . The value of A_2 reported by Schulz is $1.13 \times 10^{-3} \text{ cm}^3\text{-g.}^{-2}\text{-mole}$, which is of the same order of magnitude as our values.

Evaluation of Rate Constant k from Variation of M_w with Time

One can evaluate s , the average number of cuts per single chain, using the equation derived by Montroll and Simha,¹⁰ on a purely statistical basis for completely random degradation of long-chain molecules.

$$P_w = \alpha^2 P_0 + 2(1 - \alpha)[(1 - \alpha)^{P_0} + \alpha P_0^{-1}]/\alpha^2 P_0 \quad (1)$$

where P_w is the weight-average chain length at any stage of degradation,

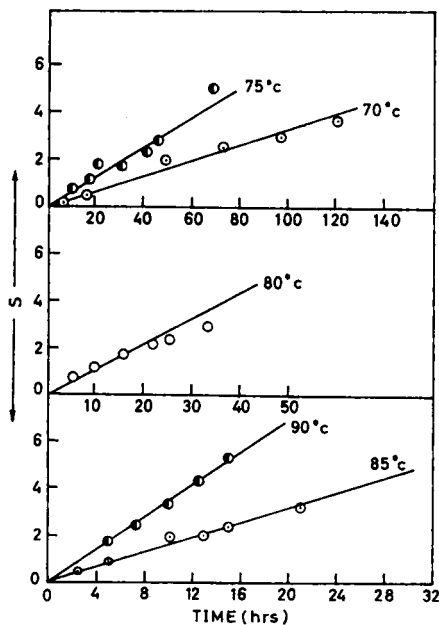


Fig. 2. Number of links broken as a function of time for rubber in cyclohexane.

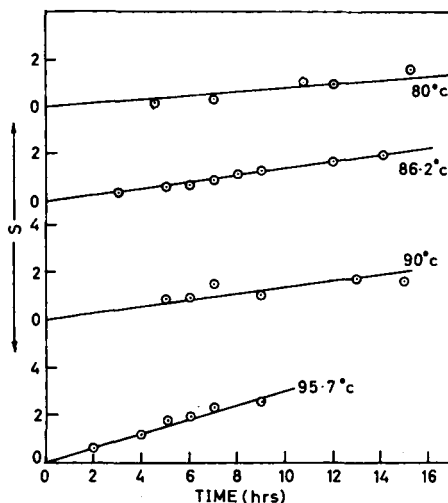


Fig. 3. Number of links broken as a function of time for rubber in *trans*-decalin.

P_0 is the initial chain length, and α is the degree of degradation. Here $\alpha = s/P_0 - 1 \approx s/P_0$ since P_0 is large.

In the early stages of the degradation, when α and s are very small, the term s/P_0 is small and, compared with unity, can be ignored. Similarly, s^2/P_0 is small compared with $e^{-s} + s^{-1}$. Under these restrictions this equation reduces to

$$P_w/P_0 = (2/s^2)(e^{-s} + s^{-1}) \quad (2)$$

which is identical with the equation deduced by Sakurada and Okamura.¹¹

It can be shown that when the rate of scission of links is proportional to the number of links present at any time, in a random process, $\alpha = kt$ where k is the rate constant and t the time.

If the plot of α the degree of degradation or s , the number of bonds broken, as a function of time is linear, only one kind of rate constant is operative; in other words, only one kind of bond is being broken.^{12,13} Some of the results are presented in Tables IV and V and illustrated graphically in Figures 2 and 3. From the figures it can be seen that the plots of s versus t are linear, proving that the degradation is taking place by the random breaking of one type of bond.

Some experiments were carried out in the presence of -0.05% pyrogallol (oxidation inhibitor) to reduce to a minimum any oxidative degradation reaction. The rate of degradation was, however, found to be the same as it was in the absence of pyrogallol. Also, the rate constants were found to be independent of the concentration of rubber in solution.

It may be noted that the rubber molecule is more extended in cyclohexane than in *trans*-decalin solution. The rate constant k is accordingly higher in the former at comparable temperatures.

TABLE IV
 Rubber-Cyclohexane Series^a

| t , hr. | P_w/P_0 | $\alpha \times 10^4$ | $k \times 10^3$ |
|-------------------------------------|-----------|----------------------|-----------------|
| At 70°C. | | | |
| 0.00 | 1.00 | — | — |
| 5.00 | 0.940 | 1.189 | 2.378 |
| 15.00 | 0.847 | 3.406 | 2.271 |
| 48.00 | 0.573 | 12.660 | 2.637 |
| 72.00 | 0.489 | 16.773 | 2.329 |
| 96.00 | 0.451 | 18.958 | 1.978 |
| 120.00 | 0.401 | 23.136 | 1.928 |
| Average $k = 2.253 \times 10^{-6}$ | | | |
| At 80°C. | | | |
| 0.00 | 1.00 | — | — |
| 5.00 | 0.797 | 4.723 | 9.446 |
| 9.00 | 0.700 | 7.551 | 8.390 |
| 15.25 | 0.602 | 11.311 | 7.417 |
| 21.50 | 0.549 | 13.785 | 6.412 |
| 25.13 | 0.527 | 14.845 | 5.906 |
| 33.00 | 0.454 | 18.701 | 5.667 |
| 48.00 | 0.251 | 43.701 | 9.104 |
| Average $k = 7.477 \times 10^{-6}$ | | | |
| At 85°C. | | | |
| 0.00 | 1.00 | — | — |
| 2.50 | 0.870 | 2.860 | 11.440 |
| 5.00 | 0.751 | 4.977 | 11.954 |
| 10.00 | 0.581 | 12.243 | 12.243 |
| 12.90 | 0.571 | 12.757 | 9.889 |
| 15.00 | 0.522 | 15.102 | 10.068 |
| 21.00 | 0.431 | 20.437 | 9.732 |
| Average $k = 10.888 \times 10^{-6}$ | | | |
| At 90°C. | | | |
| 0.00 | 1.00 | — | — |
| 5.00 | 0.603 | 11.246 | 22.42 |
| 7.33 | 0.518 | 15.360 | 20.955 |
| 10.00 | 0.417 | 21.625 | 21.625 |
| 12.50 | 0.359 | 27.699 | 22.159 |
| 15.00 | 0.308 | 33.740 | 22.493 |
| Average $k = 21.945 \times 10^{-6}$ | | | |

^a $\Delta E = 26.6$ kcal./mole.

The Calculation of the Energy of Activation

The average k values at the different temperatures are substituted in the conventional Arrhenius equation $k = Ae^{-\Delta E/RT}$ to obtain the energy of activation. A linear plot of $\log_e k$ versus $1/T$ was obtained. The values of ΔE calculated by the method of least squares are given in Tables IV and V.

The values of k at each temperature for different periods show a good agreement, at any rate with less than twofold variation. Even a tenfold variation in the value of k will change the value of the energy of activation

TABLE V
 Rubber-*trans*-Decalin Series^a

| <i>t</i> , hr. | P_w/P_0 | $\alpha \times 10^3$ | $k \times 10^6$ |
|-------------------------------------|-----------|----------------------|-----------------|
| At 80°C. | | | |
| 0.00 | 1.00 | — | — |
| 4.50 | 0.937 | 1.189 | 2.642 |
| 7.00 | 0.913 | 1.694 | 2.420 |
| 10.75 | 0.723 | 6.241 | 5.806 |
| 12.00 | 0.741 | 5.765 | 4.804 |
| 15.25 | 0.622 | 9.628 | 6.303 |
| Average $k = 4.397 \times 10^{-6}$ | | | |
| At 86.2°C. | | | |
| 0.00 | 1.00 | — | — |
| 3.00 | 0.893 | 2.140 | 7.133 |
| 5.00 | 0.827 | 3.625 | 7.250 |
| 6.00 | 0.817 | 3.923 | 6.538 |
| 7.00 | 0.758 | 5.349 | 7.641 |
| 8.00 | 0.690 | 7.311 | 9.139 |
| 9.00 | 0.676 | 7.786 | 8.651 |
| 12.00 | 0.610 | 10.104 | 8.420 |
| 14.12 | 0.571 | 11.768 | 8.336 |
| Average $k = 7.888 \times 10^{-6}$ | | | |
| At 90°C. | | | |
| 0.00 | 1.00 | — | — |
| 5.00 | 0.746 | 5.646 | 11.292 |
| 6.00 | 0.744 | 5.706 | 9.510 |
| 7.00 | 0.636 | 9.153 | 13.076 |
| 9.00 | 0.725 | 6.181 | 6.868 |
| 13.00 | 0.603 | 10.431 | 8.024 |
| 15.00 | 0.613 | 9.985 | 6.657 |
| Average $k = 9.238 \times 10^{-6}$ | | | |
| At 95.7°C. | | | |
| 0.00 | 1.00 | — | — |
| 2.00 | 0.816 | 3.923 | 19.615 |
| 4.00 | 0.681 | 7.608 | 19.020 |
| 5.05 | 0.595 | 10.758 | 21.303 |
| 6.00 | 0.578 | 11.471 | 19.118 |
| 7.00 | 0.523 | 13.938 | 19.911 |
| 9.00 | 0.510 | 14.562 | 16.180 |
| Average $k = 19.191 \times 10^{-6}$ | | | |

^a $\Delta E = 24.9$ kcal./mole.

by 1.5 kcal. only. The average energy of activation for degradation of pure rubber in the two inert solvents (cyclohexane and *trans*-decalin) is 25.8 kcal./mole. The linearity of the plots of s , obtained from eqs. (1) and (2) for random degradation, versus t , and the energy of activation of 25.8 kcal./mole, lead us to make some inferences.

The energy required to break a C—C bond is about 81 kcal./mole. The interunit C—C bond in polyisoprene may be expected to break more

easily, giving rise to isoprene and dipentene units, because in this mode of rupture two allyl radicals each with a resonance energy of 19 kcal./mole are formed. In this fashion, the energy required to break a C—C bond can be reduced to 43 kcal./mole. The measured overall E of 26 kcal./mole is significantly lower.

It is therefore reasonable to assume that the normal C—C bonds would remain unaffected and some kind of weak links are being broken, unless the normal links are converted by some process into appropriate weak links which, however, seems unlikely. Earlier workers also have postulated the existence of weak links in view of the observed low free energy of activation for degradation. Thus, Schultz et al.^{14,15} in their study on hydrolysis of nitrated cellulose observed that certain links in cellulose, about five to eight in number in a molecule of 3000 DP, hydrolyze one thousand times faster than the rest. Jellinek¹⁶ made a similar observation in his study on the degradation of polystyrene, in which he reports an energy of activation of 21.9 kcal./mole. Watson,⁶ in his study on the thermal degradation of purified crêpe rubber, reported an energy of activation of 15.9 kcal./mole and ascribed this value to the rupture of some kind of weak links.

Thus, it is generally believed that a certain kind of easily fissured bond exists in polymers, the nature of which still remains largely speculative.

In most cases in which weak links are reported the role of oxygen in their formation is emphasized. Thus Lacau and Magat⁴ in their study of the oxidative degradation of GR-S in toluene at 70–130°C. observed that there is a close relation between degradation and peroxide formation. They reported that two types of peroxide exist, the more stable of which has an energy of activation of 20–25 kcal./mole. Farmer et al.¹⁷ and Bevilacqua,¹⁸ working with oxygen derivatives of model compounds, have presented mechanisms for degradation through peroxide and hydroperoxide rupture and, in certain cases, through formation of epoxide.

However, our studies in presence of pyrogallol seem to indicate that an oxidative process was playing a minor role, if any: and the degradation was predominantly a thermal process resulting in the scission of the weak links already present in the rubber molecules. The possibility that a carbonyl type of structural defect was introduced during the biosynthesis of rubber in nature has been pointed out by Sekhar.¹⁹

The infrared spectra of sol and gel rubber that we have studied indicate the presence of epoxy groups in the rubber molecule. Peroxide groups could also be present, but because of the overlapping of the absorption due to the C=C double bond they are difficult to distinguish.

Thanks are due Dr. M. S. Narasinga Rao for many helpful discussions.

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Synopsis

The kinetics of low-temperature (60–100°C.) thermal degradation of deproteinized and deresinified petroleum ether soluble fraction of natural rubber in two chemically inert solvents, cyclohexane and *trans*-decalin, have been studied. The changes in M_w , A_2 , and $(\bar{r}^2)^{1/2}$ at various stages of degradation have been obtained from the light-scattering data. The rate constants and the energy of activation for chain scission have been calculated from the observed variation in M_w . The scission has been found to be random and the average energy of activation is 25.8 kcal./mole. This low-energy requirement suggests the presence of weak links in the rubber molecule which get ruptured at low temperature.

Résumé

On a étudié les cinétiques de dégradation thermique, à basse température (60 à 100°C), d'une fraction de caoutchouc déprotéinisé et dérésinifié, soluble dans l'éther de pétrole en présence de deux solvants inertes, le cyclohexane et la *trans*-décaline. Les données de diffusion lumineuse nous ont renseigné sur les changements de M_w , A_2 et $(\bar{r}^2)^{1/2}$ à divers degrés de dégradation. On a calculé les constantes de vitesse et l'énergie d'activation de la rupture de chaîne à partir des variations observées de M_w . La rupture de chaîne est statistique et l'énergie d'activation moyenne est de 25.8 kcal/mole. La faible énergie requise nous permet de suggérer qu'il existe des liens faibles, qui dans la molécule de caoutchouc se brisent à basse température.

Zusammenfassung

Die Kinetik des thermischen Abbaus einer eiweiss- und harzfreien, petrolätherlöslichen Kautschukfraktion wurde in zwei chemisch inerten Lösungsmitteln, Cyclohexan und *trans*-Dekalin, bei niedriger Temperatur (60–100°C.) untersucht. Die Werte für M_w , A_2 und $(\bar{r}^2)^{1/2}$ wurden für die verschiedenen Abbaustadien aus Lichtstreuungsmessungen erhalten. Aus der beobachteten Abnahme von M_w wurden Geschwindigkeitskonstanten und Aktivierungsenergie für die Kettenspaltung berechnet. Die Spaltung verläuft statistisch und die mittlere Aktivierungsenergie beträgt 25,8 kcal/Mol. Dieser niedrige Energieaufwand spricht für die Anwesenheit schwacher Bindungen in der Kautschukmolekel, die bei niedrigeren Temperatur angegriffen werden.

Received September 19, 1962