Thermal Analysis of a Poly(phenyl-*as*-triazine)

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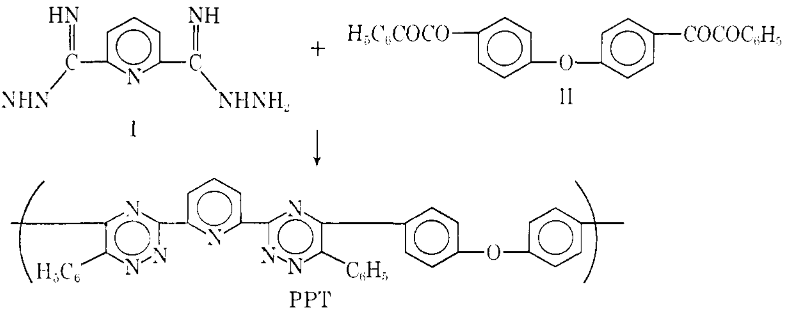
Received March 2, 1970

ABSTRACT: A well-characterized poly(phenyl-*as*-triazine) was pyrolyzed under dynamic and isothermal conditions under vacuum and in air. Simultaneous thermogravimetric, differential thermal, and thermobarometric analyses of polymer films indicate a multistage thermal decomposition. An exothermic reaction between 305 and 465° was shown to involve the asymmetric triazine ring. This leads to the formation of a stable intermediate symmetrical triazine and nitrilic products, primarily benzonitrile. The residue decomposes endothermically between 480 and 525° with the evolution of principally hydrogen cyanide and ammonia. A third decomposition region becomes apparent between 690 and 760° which is characterized by a small exotherm, attributed to dehydrogenation of the residue to yield highly condensed aromatic carbons. The apparent overall activation energy obtained from isothermal weight loss measurements between 330 and 380° was 22.5 kcal/mol. Based on these data, a degradation scheme initially involving the scission of the nitrogen–nitrogen bond in the asymmetric triazine ring was postulated.

The synthesis of high molecular weight soluble poly-*as*-triazines was recently reported.[1] Preliminary thermal stability evaluation of the poly-*as*-triazines by TGA indicated that these polymers appear to be more stable in air than in an inert atmosphere. The *as*-triazine polymers undergo thermal reactions above 300° which are not normally observed for other aromatic heterocyclic polymers.[2,3] In this work, the thermal degradation of a poly(phenyl-*as*-triazine) was studied in detail in an attempt to determine the mode of thermal breakdown.

Experimental Section

The poly(phenyl-*as*-triazine) (PPT) was prepared from the reaction of 2,6-pyridinediyldihydrazidine (I) and *p,p'*-oxydibenzil (II) as shown in eq 1 through a slight modification of a known procedure.[1]



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p,p'-Oxydibenzil (65.168 g, 0.150 mol) as a fine powder was added during 5 min to a solution of 2,6-pyridinediyldihydrazidine (28.983 g, 0.150 mol) in *m*-cresol (265 ml) at ambient temperature under nitrogen. An exotherm to 36° was observed with the formation of an orange solution. Additional *m*-cresol (110 ml) was added and the solution was stirred at 36° for 3 hr. The resulting viscous orange solution was heated to 60° and stirred at 60° for 1 hr. A portion of the *m*-cresol solution was poured into methanol in a Waring Blendor to precipitate a fibrous yellow solid which was thoroughly washed in hot methanol. After drying for 5 hr at 200°, *in vacuo*, the yellow polymer exhibited an inherent viscosity (η_{inh}, 0.5% H_2SO_4 at 25°) of 1.41 dl/g and a glass transition temperature (T_g) of 215°.

Anal. Calcd for $(C_{35}H_{21}N_7O)_n$: C, 75.66; H, 3.81; N, 17.65. Found: C, 75.57; H, 3.78; N, 17.49.

Pinhole-free lemon-yellow transparent films of uniform thickness (~1 mil) were prepared by doctoring the polymer solution (10% solids content in *m*-cresol) onto a glass plate. The solvent was removed, accompanied by further advancement of the polymer, by drying at 80° for 2 hr under nitrogen followed by heating to 200° during 2 hr and maintaining at 200° for 5 hr, *in vacuo* (<1 mm). The properties (η_{inh}, T_g, elemental analysis) of the films prepared in this manner were essentially identical with those previously reported for the yellow polymers isolated by quenching in methanol.

Apparatus. Thermal analysis was performed on a Mettler-Universal thermal analyzer which provides thermogravimetric analysis (TGA), differential thermal analysis (DTA), thermobarometric analysis (TBA), and derivative thermogravimetric analysis (DTG) simultaneously. Runs were made in a 3 × 4 mm platinium crucible to which the temperature recording thermocouple was directly attached Samples of polymer films were rolled into the crucible and remained in direct contact with the crucible throughout the run. Aluminum oxide was used as reference material for the DTA recordings.

Isothermal weight loss measurements were carried out in a Cahn electrobalance. Equilibrium sample temperatures were generally obtained within 3–4 min from the start of the measurements. Weight losses and temperature were continuously recorded on a Bristol chart recorder.

Mass spectra were obtained using a Varian M66 mass spectrometer. Recordings were made at 70 eV and 30 μA. Time in flight mass spectral analysis was performed on a Bendix Model 14-206T mass spectrometer. Film samples were placed into a pyrolysis probe which was located in the injection port of the mass spectrometer. Samples were outgassed at 10^{-6} Torr pressure prior to pyrolysis. Mass

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(1) P. M. Hergenrother, *J. Polym. Sci., Part A-1*, **7**, 945 (1969).
(2) W. Wrasidlo and R. Empey, *ibid., Part A-1*, **5**, 1513 (1967).
(3) W. Wrasidlo, *ibid., Part A-1*, **8**, 1107 (1970).

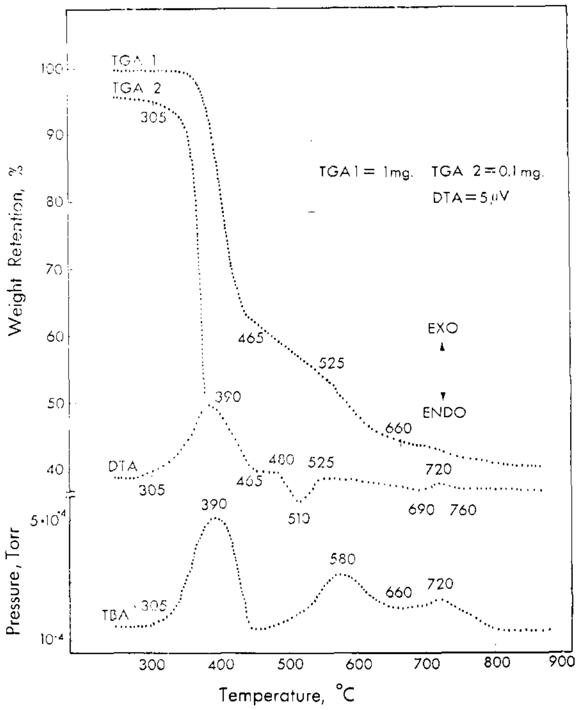


Figure 1. Thermal analysis of PPT (9.97 mg) *in vacuo*; heating rate, 10°/min.

spectra were obtained at intervals as the temperature of the samples was raised from ambient temperature to 800°.

Flash pyrolysis studies were carried out using a FM-5750 gas chromatograph (gc) to which a pyrolysis unit was attached. A pyrolysis probe (U-shaped platinum foil) containing 1–2 mg of polymer film was placed into the injection port of the chromatograph. Samples were flushed with helium gas for 1 hr prior to firing. Samples were fired for 11 sec and the volatile products were analyzed in the gc.

Results

A reproduction of the original thermogram under vacuum is shown in Figure 1. Data, especially the DTA and TBA, show three very distinct regions. Degradation is initiated at 305° and is characterized by the onset of an exothermic reaction (DTA) with simultaneous gas evolution (TBA) and consequently weight loss (TGA2). The exothermic process reaches a maximum at 390° corresponding to a pressure maximum and maximum rate of weight loss (TGA1). The exotherm and gas evolution cease at 465°. At 455° the TGA1 curve shows an abrupt change in slope corresponding to a weight loss of 36.5%. Mass spectral analysis of the volatile products from a film pyrolyzed at 390° in the injection port of the mass spectrometer (Figure 2) showed benzonitrile to be the major single component. The temperature dependence of benzonitrile formation was determined by time in flight mass spectral analysis. Figure 3 shows the relative heights of the 103 *m/e* mass peak recorded between 300 and 510°. A maximum relative concentration of benzonitrile was found to occur at about 390°.

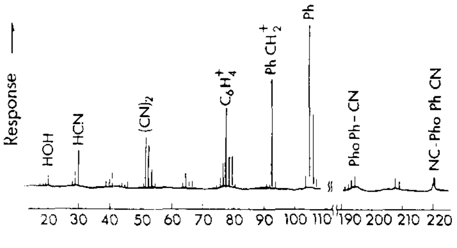


Figure 2. Mass spectral analysis of PPT pyrolyzed in injection port of the analyzer at 390°.

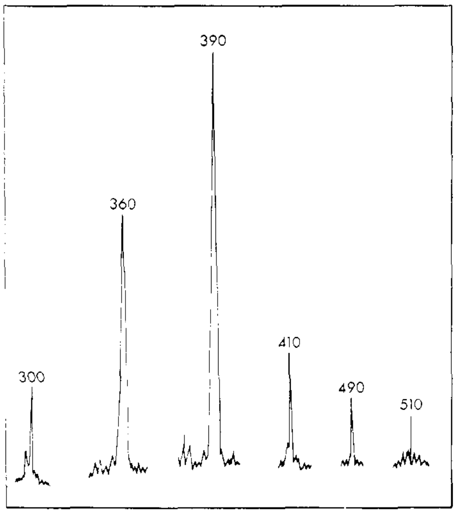


Figure 3. Benzonitrile mass peaks (*m/e* 103) at various temperatures.

The second stage of degradation occurs between 480 and 660° with an endothermic peak at 510°. The mass loss maximum from this reaction as evident from the TGA1 and TBA curve does not occur until 580°. A mass spectrum of the volatile components at this temperature is shown in Figure 4. Hydrogen cyanide and ammonia were the major nitrogeneous gases formed. The temperature dependence of hydrogen cyanide formation is shown in Figure 5. The highest mass peak was observed at 580°, the temperature at which also a TBA maximum occurred.

A third major decomposition region was observed (Figure 1) between 690 and 760°. A pressure maximum and corresponding small exotherm occurred at 720°. The mass spectrum of volatile fragments at this temperature is shown in Figure 6.

Elemental analysis of residues from fractional pyrolysis under vacuum gave the results shown in Table I. The observed elemental composition of the residue after

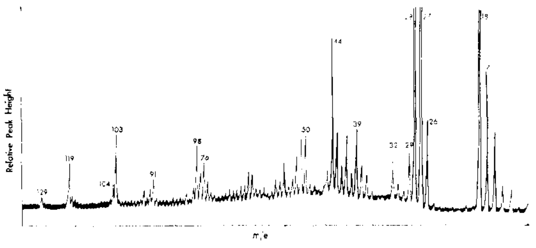


Figure 4. Mass spectral analysis of volatile fragments from pyrolysis at 580°.

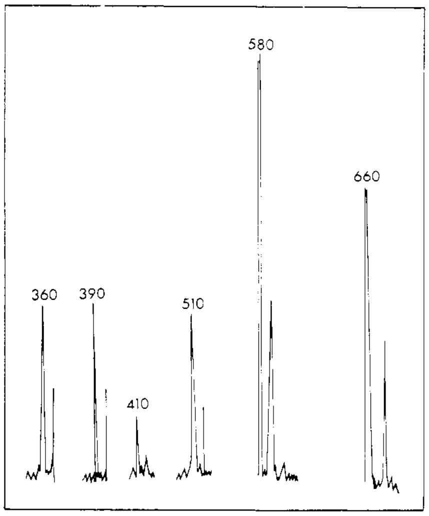


Figure 5. Hydrogen cyanide mass peaks (*m/e* 27) at various temperatures.

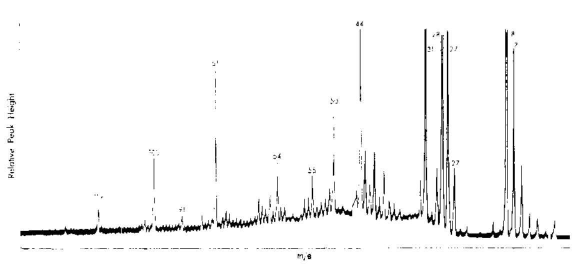


Figure 6. Mass spectral analysis of volatile fragments from pyrolysis at 720°.

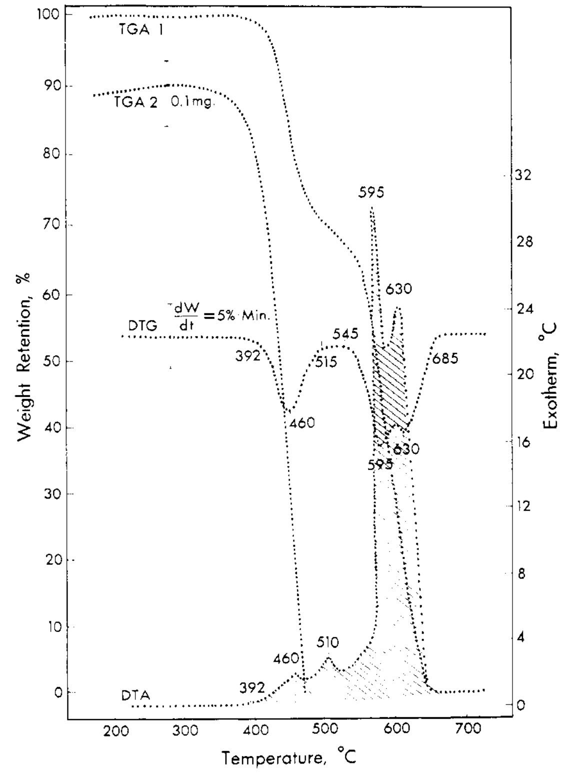


Figure 7. Thermal analysis of PPT (10.27 mg) in flowing air (5 l./hr); heating rate, 10°/min.

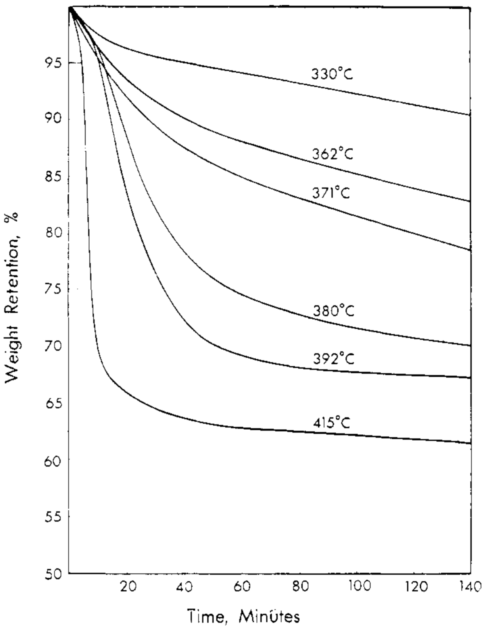


Figure 8. Isothermal degradation of PPT *in vacuo* at various temperatures.

Table I

Analysis of Residues from Pyrolysis of PPT at Various Temperatures

Temp of pyrolysis, °C	Duration, min	Residue, %	Per cent C	Per cent H	Per cent N
Original polymer	0	0	75.57	3.78	17.49
450	30	63.5	77.59	3.59	14.25
650	30	48.8	81.03	2.62	11.75
800	30	40.3	82.15	0.78	9.59

exposure to 450° under vacuum does not fit the expected CHN ratio for the loss of 2 mol of benzonitrile per repeat unit structure. Deviations in elemental composition from a theoretical residue are to be expected since the intermediate (eq 2) can recombine to form a mixture of products with different elemental compositions.

Original curves for the thermal analysis of PPT in flowing air are reproduced in Figure 7. Under the conditions specified in Figure 7 the temperature of initial decomposition determined from the onset of the DTG and DTA curves was 392°. The DTG curve showed three maximum rates of weight loss at 460, 595, and 630°. At these temperatures, there were three corresponding exotherms. In addition, an exothermic peak occurred at 510° for which no rate maximum was observed.

Isothermal degradation studies were made under vacuum using a Cahn electrobalance. Cumulative loss of weight was plotted as a function of time in Figure 8. The rate of weight loss calculated from these curves is plotted in Figure 9 as a function of volatilization which indicates two distinct degradation regions. The initial rates in the low-temperature region between 330 and 371° were high and dropped rapidly to points corresponding to 6% weight loss for the lowest

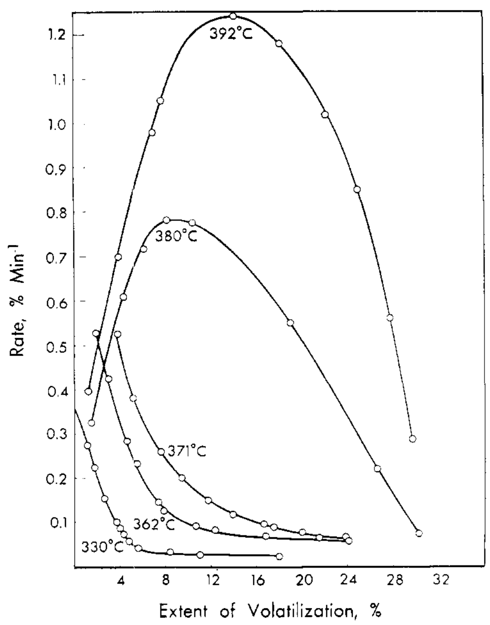


Figure 9. Rates of degradation of PPT at various temperatures.

temperature. No apparent maximum rates were observed.

In the high-temperature region between 380 and 415° the shape of the rate curves take on a completely different character, showing apparent rate maxima between 8 and 20% volatilization and relatively linear behavior beyond these maximum rates.

The temperature dependency for the reaction in the range between 330 and 380° is shown in Figure 10. The initial rates were obtained by extrapolating the linear parts of the curves in Figure 9 to the ordinate axis. From the slope of the plot in Figure 10 an activation energy of 22.5 kcal/mol was calculated for the pyrolysis in the lower temperature range.

The thermal degradation in the range between 800 and 1500° was studied by flash pyrolysis. Chromatographic analysis of gases and pyrolysis details are given in Figure 11. The major single volatile decomposition product was benzonitrile, with hydrogen cyanide, 2-cyanopyridine, 2,6-dicyanopyridine, and 4,4′-dicyanodiphenyl ether being present as minor components. The first peak in the chromatogram constitutes a mixture of light gases. As shown in Figure 11, the nature of volatile products between 800 and 1500° does not change, however, the relative amounts increase with increasing temperature.

Discussion

The exothermic decomposition of poly-*as*-triazines is unusual but has been observed with other heterocyclic polymers containing nitrogen–nitrogen bonds.[4] The exothermic portion of the DTA curve in Figure 1 is related to the formation of benzonitrile. The symmetrical shape of this curve is characteristic for first-order kinetics.[5] A weight loss of 36.5% occurs at the end of the exotherm and corresponds to the loss of 2 mol of benzonitrile/mole of repeat unit structure. The activation energy for this portion of degradation, as calculated on the basis of isothermal rates, was 22.5 kcal/mol (Figure 10). This value agrees well with the bond-dissociation energy of a single nitrogen–nitrogen bond for which a value of 20 kcal/mol has been reported.[6] A mechanism consistent with the observed data was proposed where degradation is initiated by the scission of nitrogen–nitrogen bonds in the *as*-triazine ring (eq 2). This leads initially to the formation of

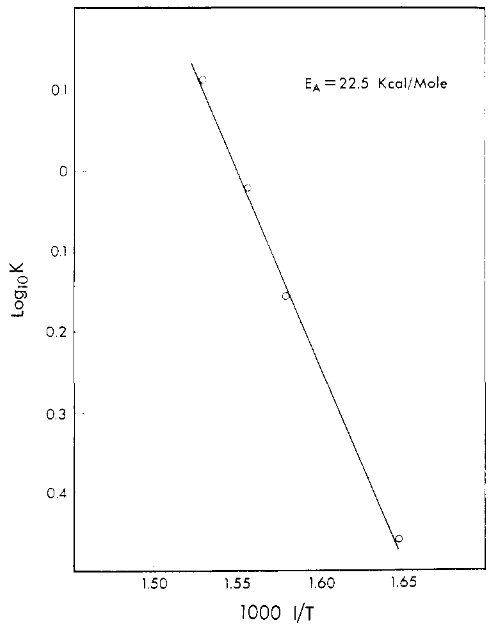


Figure 10. Arrhenius plot for the isothermal decomposition of PPT *in vacuo*.

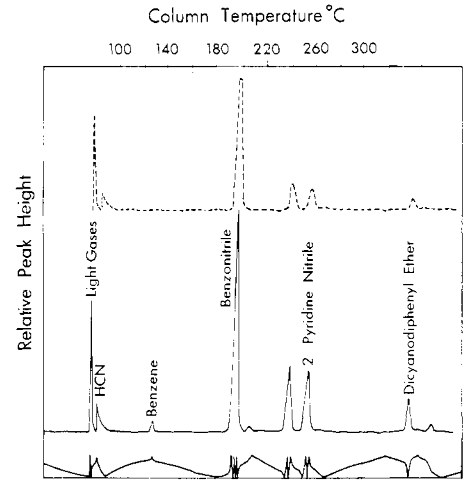
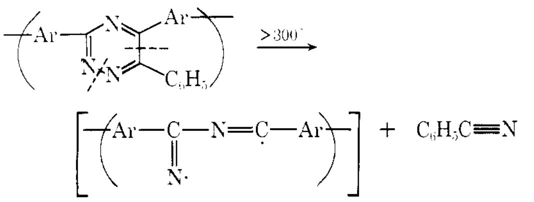


Figure 11. Gas chromatographic analysis of products from flash pyrolysis of PPT at 800° (· · ·) and 1500° (—) (column: SE-52 on Chromosorb W; heating rate of column, 20°/min; gas flow, 60 cc/min; duration of pyrolysis, 11sec).



(2)

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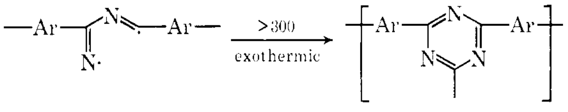
(4) A. H. Frazer and I. M. Sarasohn, *J. Polym. Sci., Part A-1*, **4**, 1649 (1966).

(5) H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).

(6) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., p 52.

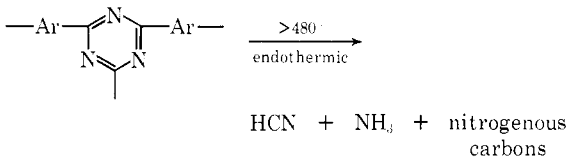
benzonitrile and pseudostable intermediates. The second step involves the recombination of nitrile radicals to form symmetrical triazine rings (eq 3).



(3)

Evidence for this reaction was obtained from mass spectral data of the decomposition products at high temperatures. A mass peak of 81 corresponding to the formation of symmetrical triazine was present in the spectra at 720° (Figure 6) but was absent in the spectra at 580° (Figure 4). Intermediate products such as the symmetrical triazine shown in eq 3 are thermally stable.[7] The formation of stable intermediate products is evident from the data in Figures 1 and 7.

Above 480° the intermediate residue decomposes endothermically with hydrogen cyanide and ammonia as the major nitrogeneous products formed. This reaction produces a maximum endotherm at 510° and maximum gas evolution at 580° (Figures 1 and 5).



A delay in mass loss from this endothermic reaction is surprising since the products formed are light gases and at these temperatures diffusion should not be rate determining. It is possible, however, that the endotherm involved fragmentation of the residue into larger species with subsequent cracking of fragments in the vapor phase. The resulting heat of vaporization could have been neutralized by the heat of decomposition of fragments thus explaining the lack of a DTA peak at the temperature of maximum gas evolution. The third major reaction takes place between 690 and 760° and reaches a maximum at 720° (Figure 1). Dehydrogenation was the major reaction in this temperature range as indicated by a 70.5% decrease in hydrogen in the elemental composition of the residue (Table I).

Degradation under oxidative conditions proceeds in two major steps (Figure 7). First the polymer decomposes thermally between 392 and 515° in a similar fashion to that under vacuum to form a stable intermediate which then oxidizes between 545 and 685° by a very strong exothermic process. The temperature of initial decomposition in air (Figure 7) was 392°, significantly higher than under vacuum (Figure 1), or in argon. Additional repetitive experiments were carried out to substantiate these findings and gave identical results. Apparently the polymer is stabilized in the presence of air by a mechanism presently not understood. This unusual stabilization phenomenon is presently under investigation.

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(7) G. F. Ehlers and J. D. Ray, *J. Polym. Sci., Part A*, **2**, 4989 (1964).

Thermal Stability of the Carbon–Carbon Cross-Linkage in Polymer Networks

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Received April 30, 1970

ABSTRACT: The thermal stability of carbon–carbon cross-linkages in elastomeric systems was studied by comparing the vacuum chemical stress relaxation of samples with different concentrations of these cross-linkages. The systems studied included silicone rubber, cross-linked polyethylenes, and Dexsil-201 rubber. Arrhenius activation energies of about 55 kcal/mol were found for the scission of these cross-linkages in the temperature range 300–350°. Cross-linkages added to a sample by additional curing were found to be, in general, more stable than those first formed. A more detailed analysis of the cleavage reaction was performed on peroxide-cured Dexsil-201 elastomer—made possible because the main chains of this material are stable at the temperatures used. Two species of cross-links were distinguishable: one having the same stability as the carbon–carbon cross-linkage in silicone rubber, another being ten times as stable and probably devoid of normal carbon–carbon bonds.

The exploration of the thermal stability of cross-linked elastomeric materials has almost necessarily paralleled the development of the techniques of chemical stress relaxation, because the more conventional methods of following chemical reactions do not lend themselves to these solid insoluble materials. Chemical stress relaxation is also one of the simplest, as well as one of the few, methods for direct, *in situ* measurement of the rate of reaction of the bonds in these intractable materials. It depends on the proportionality between the number of network chains in an elastomer and the elastic force generated by the sample on extension. The number of network chains in turn can be related to the number of scissions which occurred.[1]

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(1) A. V. Tobolsky, "Properties and Structure of Polymers," Wiley, New York, N. Y., 1960, Chapter V.