Photodegradation of Polyacrylonitrile in Solution*

H. H. G. JELLINEK

Department of Chemistry, Essex College, Assumption University of Windsor, Canada

W. A. SCHLUETER

Boeing Aircraft Company, Seattle, Washington

Investigations of the photodegradation of polymers of a fundamental nature are as yet not very numerous. In particular, a fundamental and systematic investigation of the photodegradation of polyacrylonitrile has not yet been carried out. There are a number of papers dealing with the thermal degradation of polyacrylonitrile and polymethacrylonitrile which are of interest. Some observations on the thermal stability of polyacrylonitrile were made by Grassie and Melville,[1] and pyrolysis of the polymer was investigated by Burlant and Parsons[2] and by Skoda, Schurz, and Bayszer.[3] The thermal degradation of polymethacrylonitrile was studied by Grassie and McNeill[4] and the alkaline degradation by McCartney.[5] It is noteworthy that 85% of polymethacrylonitrile is transformed to monomer on pyrolysis,[4] whereas negligible amounts of monomer are formed when polyacrylonitrile is thermally degraded[2]; also, for a small degree of destruction of polyacrylonitrile there is a marked decrease in solubility although the nitrogen content remains the same.
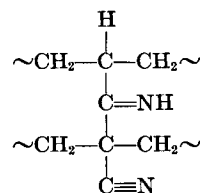
Some work has also been done on the effect of high energy radiation on polyacrylonitrile and polymethacrylonitrile.[6] Films of the two polymers were irradiated with 1-m.e.v. electrons. In the case of polyacrylonitrile in a nitrogen atmosphere, mainly crosslinking and some chain scission took place. In the presence of oxygen, however, chain scission was predominant, but some crosslinking also occurred. In contrast, polymethacrylonitrile suffers only chain scission in the presence and absence of oxygen.

The present experiments on the photodegradation of polyacrylonitrile were carried out with solutions. This has the advantage that polymer concentrations can be chosen in such a way that either cross-linking or chain scission becomes the predominant reaction. This simplifies the elucidation of the reaction mechanism. The experiments reported here were performed with fairly dilute polymer solutions.

ULTRAVIOLET ABSORPTION SPECTRUM OF POLYACRYLONITRILE

Figure 1 shows the ultraviolet absorption spectrum of polyacrylonitrile in ethylene carbonate. The absorption maximum at about 265 mμ for the polymer is quite abnormal with respect to what is known about nitrile groups. Trieber, Barndt, and Toplak[7] suspected that this maximum might be due to alien groups incorporated into the polymer or to impurities; however reprecipitation and prolonged extraction with solvents did not alter the spectrum. Further work was done by Bayszer and Stubchen.[8] These authors found that acrylonitrile polymerized without catalyst still showed the absorption maximum. Thus the conclusion is reached that this absorption maximum is characteristic of the polymer and might be due to a small amount of crosslinking (Schurz[9]):

$$\sim CH_2-\overset{\displaystyle H}{\underset{\displaystyle \underset{\displaystyle \sim CH_2-\underset{\displaystyle C\equiv N}{C}-CH_2\sim}{C=NH}}{C}}-CH_2\sim$$

It is also possible that a structure postulated by Burlant and Parsons[2] for the first stages of the thermal degradation is responsible for the absorption:
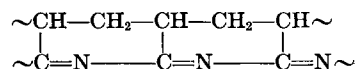
$$\sim CH-CH_2-CH-CH_2-CH\sim$$
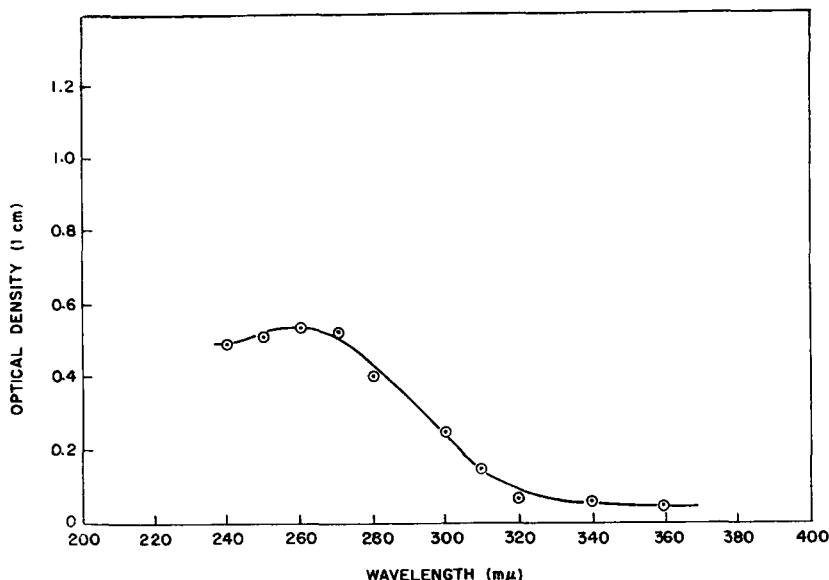$$\sim C=N-\!\!\!-\!\!\!-C=N-\!\!\!-\!\!\!-C=N\sim$$

Fig. 1. Ultraviolet absorption spectrum of 1% (w/v) solution of polyacrylonitrile in ethylene carbonate.

EXPERIMENTAL

(a) Apparatus

The apparatus consisted essentially of a constant temperature bath provided with a circular quartz window. The thermostat was rigidly located on a steel base which carried also an optical bench. The light source, diaphragms, filters, and a biconvex quartz lens (diameter 7.6 cm., focal length 10 cm.) were located on this bench. Reaction vessels and any other necessary equipment could be mounted along the entire length of the bath on a rail. Reaction vessels were made of Ultrasil quartz and were provided with ground glass joints. The light transmission of this material for a thickness of 1 cm. is nearly 100% in the wavelength region from 3000 to 2500 A. and decreases to 95% at 2250 A.

A low-pressure mercury vapor lamp was made for this work by the Hanovia Lamp Division. It consists of a 3-mm. i.d. quartz tube wound in a flat spiral of an overall diameter of 5 cm. The lamp operates at not more than 600 R.M.S. volts and carries 30 ma. The total light output was estimated by the manufacturers to be about 3×10^{18} to 5×10^{18} quanta/sec. Not less than 95% of this light output takes place at a wavelength of 2537 A. In order to stabilize the lamp current and voltage, the input to the high-voltage transformer of the lamp was taken from a constant 115-v. transformer. The lamp intensity could be kept constant within

±5%; the variation of the intensity is believed due mainly to fluctuations in the room temperature.

All ultraviolet absorption spectra were measured on a Beckman spectrophotometer (Model DU).

Intrinsic viscosities of the polymer samples were determined in Ostwald-Fenske viscometers. The measurements were performed at $25 \pm 0.1°C$. All intrinsic viscosities are expressed as $(g./100 \text{ ml.})^{-1}$

(b) Materials

Polyacrylonitrile was supplied by the Chemstrand Corporation and was obtained by thermal polymerization without catalyst.

Preliminary experiments were carried out in ethylene carbonate as solvent which had to be especially purified. However, for later experiments a mixture consisting of 80% ethylene carbonate and 20% propylene carbonate by weight was used. This mixture could be kept liquid near 20°C., whereas ethylene carbonate melts at about 35°C. The use of ethylene carbonate as solvent would have necessitated that all work be carried out at 40°C., this would have introduced complications due to thermal degradation.

The purification procedure for the solvent was as follows. Ethylene carbonate was melted and then dissolved in 95% ethanol. The solution was cooled to about 10°C., and the crystals which formed were separated by filtration. These crystals were then melted and the process repeated. Finally, the crystals were melted and the remaining ethanol dis-

tilled off under vacuum. Propylene carbonate was purified by repeated passing through charcoal.

(c) Preliminary Experiments

Preliminary experiments with 1% (w/v) solutions of polyacrylonitrile in ethylene carbonate were carried out in the presence of air and also in a nitrogen atmosphere (99.996% N_2). The solutions were exposed to radiation of 2537 A. for 4 hr. at 40°C. For these preliminary experiments flow times of the solutions in Ostwald-Fenske viscometers were taken as an indication of the extent of degradation. Some of the results are given in Table I.

TABLE I
Irradiation of 1% (w/v) Solutions of Polyacrylonitrile in Ethylene Carbonate at 40°C. for 4 Hr.
(Hanovia Lamp, 2537 A.)

Sample number	Flow time before exposure, sec.	Flow time after 4-hr. exposure, sec.[a]	
		In air	In N_2
Solvent	91.7	91.7	
Solvent	91.7	91.4	
1	356.8	236.1	
2	356.8	338.7	
3	357.9	—	340.8
4	357.9	—	352.8

[a] All flow times were measured within 1 hr. after completion of exposure.

It is seen that degradation is more pronounced in the presence of oxygen. It was also ascertained that there is an after effect (dark reaction) persisting for quite considerable periods of time after cessation of exposure, the solution being kept at 40°C. For example, the flow time of sample 2 in Table I decreased after two days from 338.7 to 335.8 sec.; after a further ten days, the flow time had decreased to 330.3 sec. In the case of irradiation in a nitrogen atmosphere, the flow time for sample 4 changed from 352.8 to 355.0 sec. after 24 hr.; seven days later the flow time had increased to 364.2 sec. In the case of unexposed solutions, a slight thermal degradation seems to proceed at 40°C.; thus, after standing for nine days in the presence of air, the flow time decreased from 341.7 to 340.4 sec. Some thermal degradation may also have taken place on dissolution of the polymer in ethylene carbonate at 40°C.

These preliminary experiments indicate that in the presence of oxygen, chain scission seems to be predominant, whereas in the absence of oxygen chain scission and some crosslinking, or at least some recombination of fragments, occurs.

(d) Experiments in Vacuo

All further experiments were carried out with 0.200% (w/v) solutions of polyacrylonitrile in a mixture of 80% ethylene carbonate and 20% propylene carbonate by weight at 25 ± 0.1°C. These solutions were freed from oxygen in a high vacuum system (10^{-6} mm. Hg) by repeated freezing, melting, and evacuating. The solutions were sealed off the high vacuum system and exposed to ultraviolet light of wavelength 2537 A. for definite periods of time. After exposure, the reaction vessels were opened, and a few crystals of benzoquinone were added; this completely eliminated any dark reaction. Subsequently the intrinsic viscosities of the exposed solutions were measured.

The intrinsic viscosities were converted into number-average chainlengths as follows. According to Onyon[10] the relationship between the intrinsic viscosity and the number-average molecular weight $\bar{M}_n$ of polyacrylonitrile in N,N-dimethylformamide solution is given by

$$[\eta] = 1.97 \times 10^{-3} \bar{M}_n^{0.62b} \qquad (1)$$

It is to be expected that the relationship for polyacrylonitrile dissolved in the ethylene carbonate–propylene carbonate mixture is of a similar form, $[\eta] = K\bar{M}_n^{\alpha}$, where K and α are empirical constants. For two polymer samples with different number-average molecular weights, one obtains, for solutions in the carbonate mixture E

$$\alpha_E = \log ([\eta]_{E_1}/[\eta]_{E_2})/\log (M_{n_1}/M_{n_2}) \qquad (2)$$

The number-average molecular weights can be obtained from eq. (1) and hence α_E can be calculated once intrinsic viscosities have been determined; the value for K_E can then be obtained easily.

Experimental results for three samples of polyacrylonitrile of different molecular weights are given in Table II. Number-average molecular weights were calulated from eq. (1).

TABLE II
Number-Average Molecular Weights for Polyacrylonitrile and Intrinsic Viscosities in Dimethylformamide (D) and Ethylene Carbonate–Propylene Carbonate (E) (80/20 by weight) Solutions at 25°C.

$\bar{M}_n$	$[\eta]_D$	$[\eta]_E$
76,000	2.19	1.65
36,000	1.40	1.21
16,000	0.81	0.78

The following values for α_E were derived: from the first two samples, $\alpha_E = 0.428$; from the first and

third samples, $\alpha_E = 0.470$; and from the second and third samples, $\alpha_E = 0.498$; this gives an average value of $\alpha_E = 0.47$.

The values of K_E for the three samples are 8.9×10^{-3}, 9.0×10^{-3}, and 8.8×10^{-3}, respectively, which yield an average value for $K_E = 8.9 \times 10^{-3}$. Hence the following relationship is obtained for the ethylene carbonate–propylene carbonate solvent mixture:

$$[\eta]_E = 8.9 \times 10^{-3} \bar{M}_n^{0.47} \qquad (3)$$

Equation (3) has been used for the conversion of all intrinsic viscosities to number-average molecular weights or chainlengths. This procedure neglects change in size distributions but will give quite good an approximation.

Next, the degradation was studied as a function of the light intensity. The intensity was varied by inserting a cylindrical quartz cell, 5 cm. in length, containing aqueous solutions of nickel sulfate in front of the reaction cell. The light transmissions for a wavelength of 2537 A. for the solutions used are given in Table III.

TABLE III

NiSO$_4$·6H$_2$O concn., g./l.	% Transmission (5 cm.)
120	79
350	63
500	56

This filter was described by Kasha[11] and proved extremely light stable; thus no change in transmission was observed after 140 hr. exposure. Degradation experiments were carried out using these solutions so that in addition to the original light intensity I_0, experiments were carried out at intensities $0.79I_0$, $0.63I_0$, and $0.56I_0$. All solutions were kept at $25 \pm 0.1°C$. during exposure, and the concentration of polymer was in all cases 0.200% (w/v). The intrinsic viscosities plotted as a function of time of exposure are shown in Figure 2.

The quantum yield was determined with a chemical actinometer as described by Leighton and Forbes[12] and Forbes and Heidt.[13] The method depends on the photochemical decomposition of oxalic acid in the presence of uranyl ions as sensitizing agents. A quartz vessel 5 cm. in length was used, containing a solution $0.005M$ in oxalic acid and $0.001M$ in uranyl oxalate. The concentration of the polymer solutions was in this case 0.300% (w/v). It was found that in 120 min. 4.3×10^{19} quanta passed through the solvent mixture into the actinometer solution, and that for the same period of time 8.8×10^{18} quanta were absorbed by the polymer solution (23 ml. of the 0.300% (w/v) polymer solution were exposed). During the same time interval, the intrinsic viscosity decreased from 1.65 to 1.63. The quantum yield was then obtained as follows. The average number of bonds broken s for each original chain is given by[14]
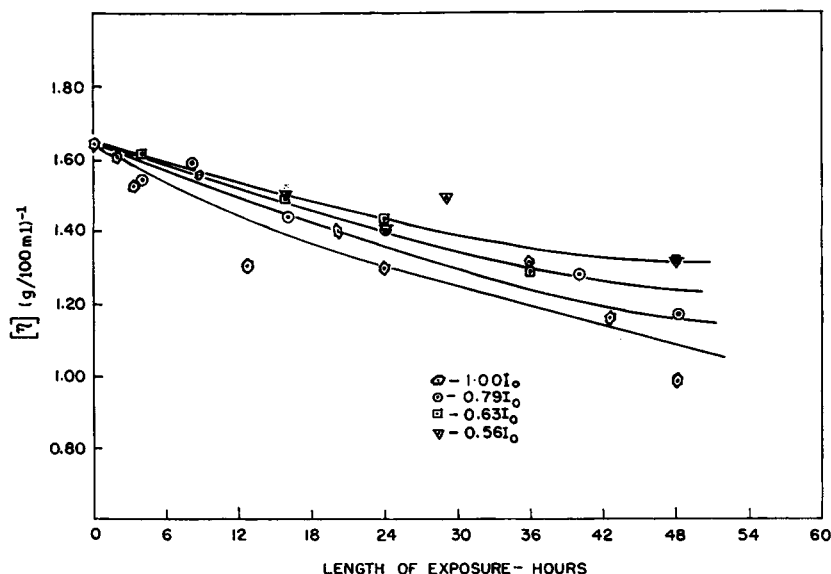
$$s = (P_0/P_t) - 1 \qquad (4)$$

Fig. 2. Intrinsic viscosity of polyacrylonitrile solutions in ethylene carbonate-propylene carbonate solution (80/20 by weight) vs. length of exposure at different light intensities.

where P_0 is the original number-average chain-length, and P_t is the number-average chainlength at time t. This value is obtained experimentally. The total number of original polymer chains in the system (all chains assumed to be of length P_0) is also known, and thus the total number of broken bonds for a given time of irradiation can be calculated. The number of quanta absorbed for the same time of exposure is known from experiment. It was found that 7.7×10^{-4} bonds are broken for each light quantum absorbed for a wavelength of 2537 A. A high accuracy is not claimed for the actual value of the quantum yield; however it is certain that the quantum yield is very small.

Infrared spectra of irradiated samples were also investigated. No difference in the infrared spectra of exposed and unexposed polymer could be detected. The polymer was precipitated from solution by water, was dried and then suspended in mineral oil; the suspension was placed between sodium chloride plates.

A change took place in the ultraviolet spectra on exposure; the maximum absorption increased with length of exposure. This will be further investigated.

DISCUSSION

The present results will be discussed in the light of the random theory of breaking links. This is quite a reasonable assumption for the present case. The rate of breaking bonds may simply be assumed to be proportional to the number of carbon-carbon bonds in the main polymer chains in the system

$$dn/dt = k'In \tag{5}$$

where n is the total number of C—C bonds in the polymer chains at time t, k' is a rate constant, and I the ultraviolet light intensity. From eq. (5) a relationship can be derived in terms of the initial number-average chainlength P_0 and the number-average chainlength P_t at time t (see Jellinek[14])

$$-\ln\,[1 - (1/P_t)] = k'It - \ln[1 - (1/P_0)] \tag{6}$$

P_0 and P_t are large numbers as the degradation is not very extensive. Hence eq. (6) reduces to

$$(1/P_t) - (1/P_0) = k'It \tag{7}$$

Figure 3 shows the plot of $(1/P_t) - (1/P_0)$ against time for the different light intensities. The experimental points show considerable scatter, but can best be represented by straight lines, which were obtained by the method of least squares. The rate constants $k = k'I$ (hours^{-1}) derived from the slopes of the straight lines are plotted against the light intensities in Figure 4. A straight-line relationship is obtained. The theory of random breaking describes, on the whole, the experimental results quite satisfactorily, though further investigation is desirable in order to ascertain whether some cross-linking takes place under these conditions. The quantum yield of 7.7×10^{-4} bonds broken for each quantum absorbed agrees with a random degradation process. The energy supplied by the light
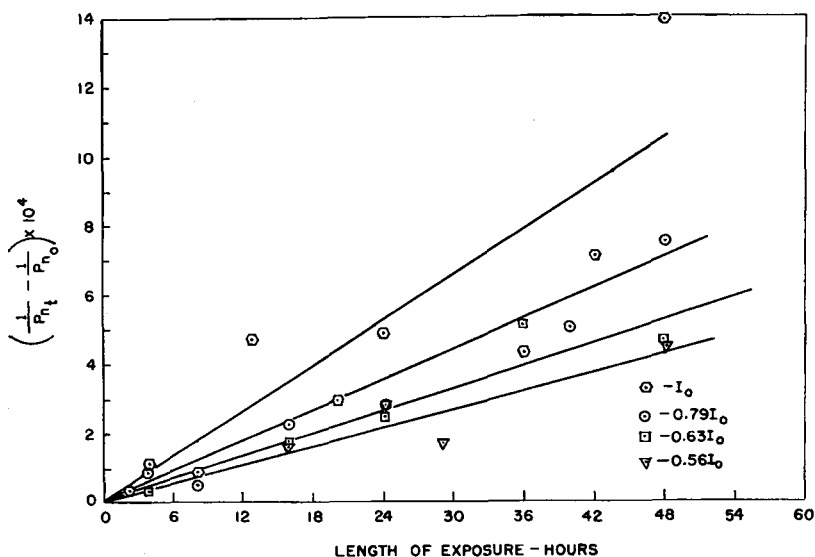

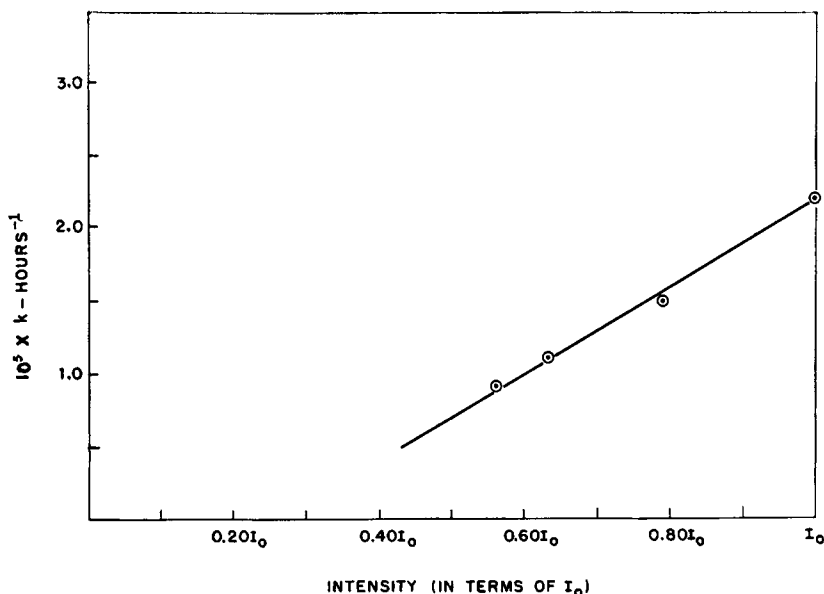Fig. 3. Plot of $(1/P_{n0}) - (1/P_{n0})$ vs. length of exposure at different light intensities.

Fig. 4. Rate constant k as a function of light intensity.

quanta is only very rarely redistributed in the chain molecules in such a way that C—C bonds are broken. Preliminary results indicate that amounts of monomer or very small chain fragments produced during degradation are negligible. Some tentative suggestions as to possible reactions leading to chain scission are given below.
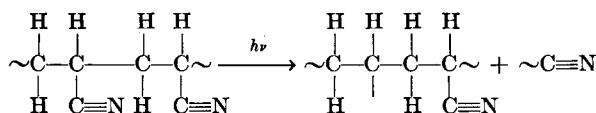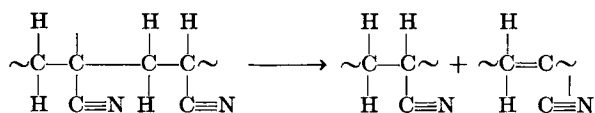
This reaction can lead to chain scission
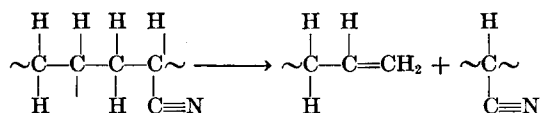
The C≡N radical could react with α hydrogen atoms leading to further chain scission:
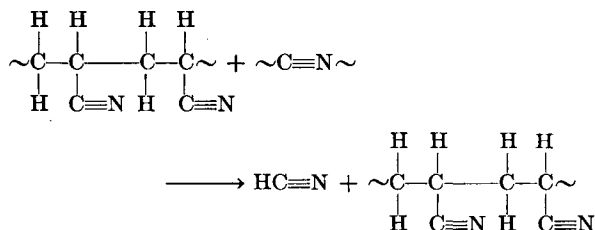
and

If, in addition to a first-order termination process, recombination of radicals also takes place, then the rate of breaking bonds becomes

$$-dn/dt = (k_3/2)n^* = k_1 In - (k_2/2)n^{*2} \quad (8)$$

where n^* is the number of radical chain ends in the system.

Further,

$$+dn^*/dt = 2k_1 In - k_2 n^{*2} - k_3 n^* \quad (9)$$

For the stationary state one has

$$k_1 In - (k_2/2)n^{*2} = (k_3/2)n^*$$

or

$$n^* = k_2 \pm [k_2^2 + 4k_1 In k_3]^{1/2}/2k_3$$

Finally,

$$-dn/dt = k_2 \pm [k_2^2 + 4k_1 In k_3]^{1/2}/4 \quad (10)$$

Thus, the simple relationship given by eq. (5) would no longer hold.

References

1. Grassie, N., and H. W. Melville, *Proc. Roy. Soc. (London)*, **A199**, 1, 14, 24, 39 (1949).

2. Burlant, W. J., and J. L. Parsons, *J. Polymer Sci.*, **22**, 249 (1956).

3. Skoda, L., J. Schurz, and H. Bayszer, *Z. physik. Chem. (Leipzig)*, **210**, 35 (1959).

4 Grassie, N., and I. C. McNeill, *J. Polymer Sci.*, **27,** 207 (1958).

5. McCartney, J. R., *Modern Plastics*, **30,** 118 (1953); *Natl. Bur. Standards Circ. 525*, 1953.

6. Burlant, W. J., and C. R. Taylor, *J. Phys. Chem.*, **62,** 247 (1958).

7. Trieber, E., W. Barndt, and H. Toplak, *Angew. Chem.*, **67,** 69 (1955).

8. Schurtz, J., H. Bayszer, and L. Stubchen, *Makromol. Chem.*, **23,** 152 (1957).

9. Schurz, J., *J. Polymer Sci.*, **28,** 438 (1958).

10. Onyon, P. F., *Trans. Faraday Soc.*, **52,** 80 (1956).

11. Kasha, M., *J. Opt. Soc. Am.*, **38,** 929 (1948).

12. Leighton, W. G., and G. S. Forbes, *J. Am. Chem. Soc.*, **52,** 3139 (1930).

13. Forbes, G. S., and L. J. Heidt, *J. Am. Chem. Soc.*, **56,** 2363 (1934).

14. Jellinek, H. H. G., *Degradation of Vinyl Polymers*, Academic Press, New York, 1955, p. 21.

Synopsis

The ultraviolet photodegradation of polyacrylonitrile was studied at 25°C. with irradiation with light of wavelength 2537 A. Polymer dissolved in a 80%/20% mixture by weight of ethylene carbonate and propylene carbonate was irradiated. Preliminary experiments indicated that in the presence of oxygen predominantly chain scission takes place, whereas in its absence chain scission and recombination of radicals seem to occur. There is also a dark reaction which proceeds for appreciable periods of time after exposure. Quantitative studies were performed *in vacuo* at 25°C. in the ethylene carbonate–propylene carbonate mixture as solvent. Degradation was followed by determining intrinsic viscosities as a function of time at various light intensities. The quantum yield was found to be 7.7×10^{-4} chain scissions for each quantum absorbed under the given experimental conditions. Infrared spectra of original and irradiated polymer samples indicate that there is no change in the overall structure of the polymer chains. The experimental results can be satisfactorily represented by the theory of random breaking of bonds assuming that the rate of breaking bonds is proportional to the number of bonds present at any time t and to the light intensity. The experimental rate constants derived on the basis of the random theory were actually found to be linearly dependent on the light intensity.

Résumé

On a étudié la photodégradation par la lumière ultra violette du polyacrylonitrile à 25°C en utilisant la longueur d'onde 2537 Å. On a irradié le polymère dissous dans un mélange 80%/20% en poids de carbonate d'éthylène et de propylène carbonate. Des expériences préliminaires montrent qu'en présence d'oxygène c'est surtout une scission de chaîne qui a lieu tandis qu'en absence d'oxygène il semble y avoir scission de chaîne et recombinaison des radicaux. Il y a aussi un post-effet pour des périodes appréciables de temps après exposition. Des études quantitatives ont été effectuées sous vide à 25°C en utilisant le mélange carbonate d'éthylène–carbonate de propylène comme solvant. La dégradation a été suivie par la détermination des viscosités intrinseques en fonction du temps à différentes intensités lumineuses. Le rendement quantique a été trouvé égal à 7.7×10^{-4} scissions de chaîne par quantum absorbé dans les conditions expérimentales données. Les spectres infrarouges du polymère avant et après irradiation montrent qu'il n'y a pas de changement dans la structure des chaînes polymériques. Les résultats expérimentaux peuvent être représentés d'une facon satisfaisante par la théorie de la rupture statistique des liaisons en admettant que la vitesse de rupture des liaisons est proportionnelle au nombre de liaisons présentes au temps t et à l'intensité de la lumière. Actuellement on a trouvé que les constantes de vitesse expérimentales obtenues à partir de la théorie statistique dépendent d'une façon linéaire de l'intensité lumineuse.

Zusammenfassung

Der Abbau von Polyacrylnitril im ultravioletten Licht wurde bei 25°C mit Licht von der Wellenlänge 2537 Å untersucht. Das Polymere wurde in einer Äthylenkarbonat–Propylenkarbonatlösung mit einem Mischungsverhältnis 80:20 Gewichtsprozent bestrahlt. Vorversuche zeigten, dass in Gegenwart von Sauerstoff überwiegend Kettenspaltung stattfindet, während in Sauerstoffabwesenheit Kettenspaltung und Radikalrekombination einzutreten scheint. Auch eine Dunkelreaktion ist vorhanden, die noch während beträchtlicher Zeiträume nach der Belichtung vor sich geht. Quantitative Untersuchungen wurden im Vakuum bei 25°C unter Benützung der Äthylenkarbonat–Propylenkarbonatmischung als Lösungsmittel ausgeführt. Der Abbau wurde durch Bestimmung der Viskositätszahl in Abhängigkeit von der Versuchsdauer bei verschiedenen Lichtintensitäten verfolgt. Under den gewählten Versuchsbedingungen wurde die Quantenausbeute zu $7,7 \times 10^{-4}$ Kettenspaltungen pro absorbiertes Quant bestimmt. Die Infrarotspektren des ursprünglichen und des bestrahlten Polymeren zeigen, dass keine Änderung der Gesamtstruktur der Polymerketten auftritt. Die Versuchsergebnisse lassen sich durch die Theorie der statistischen Spaltung von Bindungen befriedigend unter der Annahme wiedergeben, dass die Geschwindigkeit der Bindungsspaltung der Anzahl der zu einer beliebigen Zeit t vorhandenen Bindungen und der Lichtintensität proportional ist. Die experimentellen Geschwindigkeitskonstanten, die auf Grundlage der statistischen Theorie abgeleitet wurden, ergaben tatsächlich eine lineare Abhängigkeit von der Lichtintensität.