Ultraviolet Irradiation of Poly(ethyl Acrylate) in Vacuum.
I. Swelling, Solubility, and Viscosity*

HARVEY JACOBS and RICHARD STEELE

Textile Research Laboratory, Rohm and Haas Co., Philadelphia, Pennsylvania

The effect of ionizing radiation on acrylates and methacrylates has been more or less systematically studied,[1,2] but the effect of ultraviolet irradiation has been only lightly explored. In fact, little is known of the effect of ultraviolet light of relatively short wavelength, 200–300 mμ, on polymer films in general. The results of exposure to ultraviolet light for polymeric materials, such as natural and synthetic resins, rubber, textile, and paper products, have long been known.[3] However, this knowledge was mainly of a qualitative nature, the results of investigations seeking to examine gross changes in physical properties due to natural or accelerated weathering. The discovery that ionizing radiation could lead to crosslinking of certain polymers,[4] notably polyethylene, has stimulated a number of studies with ultraviolet light. Oster[5] has compared the effects of ultraviolet (200–300 mμ) and high energy electron radiation on the rate of crosslinking and main-chain fracture in polyethylenes of various degrees of crystallinity in the presence of air. The two reactions occurred to similar extents with ultraviolet light, which can only cause excitation, and with radiation of energy sufficient to cause ionization. He also reported[6] that ultraviolet light crosslinks poly(methyl methacrylate), polyisobutylene, and polypropylene in the presence of sensitizers. Cowley and Melville[7] have found that at elevated temperatures, 160–200°C., poly(methyl methacrylate) undergoes rapid degradation by depolymerization when irradiated with ultraviolet light at 2537 A. Crosslinking in poly(vinyl chloride) films by ultraviolet irradiation is described in a recent note.[8] Gel content was found to increase with increasing temperature of irradiation and to decrease with increasing film thickness. Degradation due to ultraviolet light has been reported for poly(vinyl chloride) in air[9]

and for polystyrene in air at 60°C.[10] The behavior of rubber has been investigated to a relatively greater extent.[11] When exposed in solution or bulk to ultraviolet light, rubber undergoes gelation or insolubilization by crosslinking.[12,13] Cellulose and films of its acetate and nitrate have been irradiated in oxygen and nitrogen.[14,15] The chain scission which the photo-reaction causes depends on the presence of oxygen. No insolubilization was reported. In summary, it appears that, depending on the polymer and the atmosphere, ultraviolet irradiation can cause crosslink formation, scission, or both.

Irradiation of films of poly(ethyl acrylate) with ultraviolet light in the absence of oxygen has been found to result in both scission and crosslinking, and in this paper these reactions are studied through the swelling, solubility, and viscosity changes which occur. A subsequent paper will deal with the mechanisms of the reactions.

Swelling measurements on the crosslinked polymer were used to estimate degree of crosslinking from the Flory-Rehner theory[16] and, in connection with this, an estimate was made of the thermodynamic interaction constant for the poly(ethyl acrylate)–acetone system. Also the degree of crosslinking obtained and the ratio of the rate of scission to that of crosslinking have been determined from solubility data by using Charlesby's theory.[17] Our results show the theories to be in satisfactory agreement in the case of poly(ethyl acrylate) when used to calculate crosslink contents less than 10^{-5} moles of crosslinked units per cm.^{3}.

Experimental

Poly(ethyl acrylate) was prepared by an emulsion technique with a redox catalyst and an octyl phenol ethylene oxide condensate as a dispersant. The polymer was isolated by dissolving the emulsion in acetone and pouring the solution into a large volume of water with vigorous stirring. The rub-
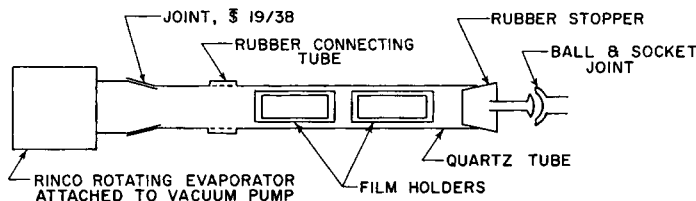
Fig. 1. Irradiation apparatus.

bery polymer curd was rinsed and dried in a vacuum desiccator at room temperature. It was then further purified by redissolving it in acetone and re-precipitating it. Films were prepared by casting ethylene dichloride solutions of the polymer on a mercury surface and allowing the solvent to evaporate slowly over a period of 3 to 7 days. The soft, tacky films were stored and handled between 3-mil sheets of Teflon. Samples for irradiation were prepared by die-cutting a strip measuring 2.5 × 0.25 in. from the Teflon sandwich. The Teflon could be easily removed without distorting the acrylate film by chilling the specimen with solid carbon dioxide.

The irradiation was carried out with the apparatus shown in Figure 1. Films 10 mils thick were held in aluminum frames in a quartz tube mounted 2 in. from a Sylvania germicidal lamp. Such lamps are near-monochromatic sources since about 95% of their radiation is at 254 mμ. The quartz tube was attached to a vacuum pump, which maintained the pressure at about 0.1 mm., through a Rinco Rotating Evaporator turning at 3 rpm, so that both sides of the film were irradiated. There appeared to be no temperature rise due to the lamp. Room temperature, about 26°C., was the temperature of the experiment.

After being irradiated, the films were put into reagent grade acetone for swelling ratio and gel content measurements, the solvent/sample volume ratio being greater than 500/1. The extraction time was 48 hr. or longer and the solvent was replaced at least once during this time. The swelling ratio was determined from the weight of polymer before and after extraction and from a measured dimension before irradiation and after extraction, the latter being made while the film was still under acetone. The relationship used was

$$q_{2m} = (W_0/W)(l_1/l_0)^3$$

where q_{2m} is the swelling ratio; W_0 and W represent the weight in grams before irradiation, and after irradiation and extraction, respectively; and l_0 and l_1 are a dimension of the film before and after swelling, respectively. Swelling was shown to be

isotropic, and it was assumed that the density of the polymer did not change during irradiation. The gel content (g) was determined from the weight of the polymer, dried at about 50°C. after extraction, and its original weight.

The intrinsic viscosity of the polymer before irradiation and of the soluble fraction after irradiation was determined with a Cannon-Ubbelohde dilution viscometer. Solution concentrations were obtained from the weight of residue remaining after evaporating a known volume of solution.

The swelling ratio data have been examined according to the equation given by Flory and Rehner.[16]

$$-[\ln (1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}{}^2]$$
$$= v_1(\nu_e/V_0)(v_{2m}{}^{1/3} - v_{2m}/2)$$

The moles of effective network chains per unit volume of the undeformed polymer network (ν_e/V_0), are calculated according to this equation from the reciprocal of the experimental swelling ratio, v_{2m}. The remaining terms are constants, v_1 being the molar volume of the solvent and χ_1, the thermodynamic interaction constant. Values of 0.43 (ref. 18) and 0.46 (ref. 19) have been determined for χ_1 from osmotic pressure data.

The gel content data have been examined according to the method of Charlesby[17] which treats gel content as a function of the dose of ionizing radiation. It has been assumed that the theory will fit ultraviolet irradiation as well as ionizing irradiation. Adopting the notation of Charlesby, the relation of weight fraction soluble material, $s = 1 - g$, to the number of crosslinked units δ'', per instantaneous primary weight average molecule is:

$$s = [1 + \delta''g/2]^2$$

where g is the gel weight fraction. The relation of δ'' to δ, the number of crosslinked units per original primary weight-average molecule is:

$$\delta = R/R_0{}^* = \delta''/[1 - (\beta/2\alpha)\delta'']$$
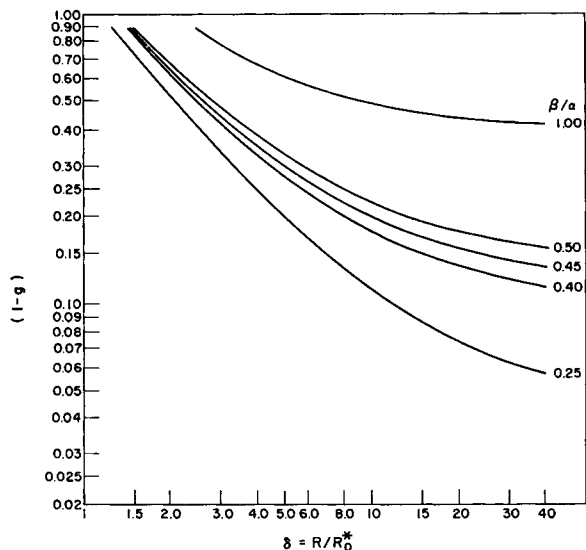$$0 \leqslant \delta'' \leqslant 2\alpha/\beta$$

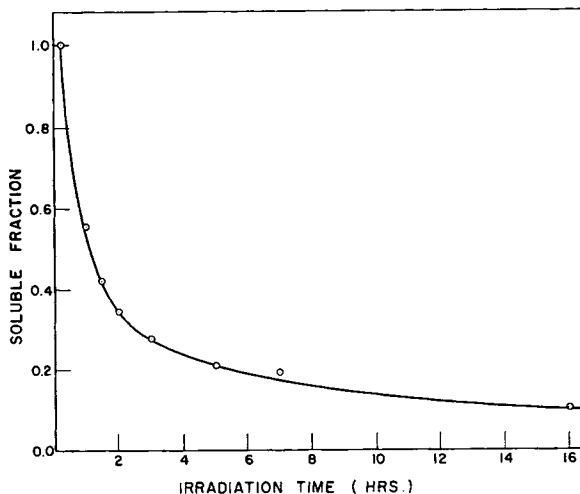Fig. 2. Theoretical curves according to the Charlesby equation.

Fig. 3. Solubility of poly(ethyl acrylate) after ultraviolet irradiation.
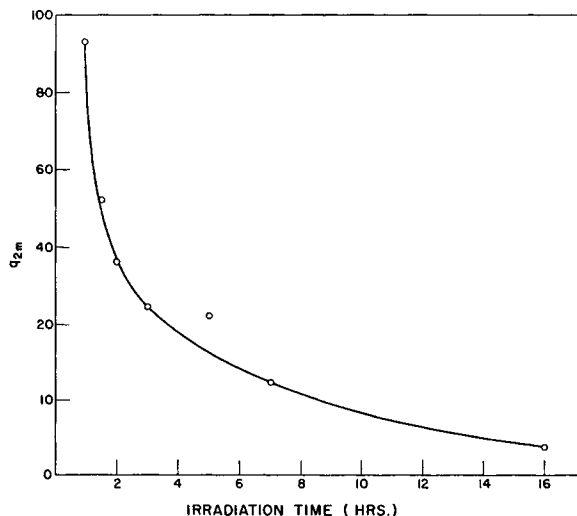
Fig. 4. Swelling ratio of poly(ethyl acrylate) after ultraviolet irradiation.

β/α is the ratio of the number of main-chain fractures produced to the number of crosslinked units formed. The radiation dose is R, which we have taken as the time of irradiation, and $R_0{}^*$ is the incipient gelation dose, the time of irradiation to produce incipient gelation if no main-chain scissioning has occurred. These two equations yield a family of curves connecting s and δ, each curve corresponding to a given value of β/α, as shown in Figure 2. The ratio β/α and $R_0{}^*$ are determined by superimposing experimental data for s and R upon the theoretical plot and shifting the experimental curve along the δ axis until a satisfactory fit is obtained. The curve which fits best determines β/α, and the distance moved along the δ axis corresponds to $R_0{}^*$ since log-log coordinates are used.

Results

Films of poly(ethyl acrylate) have been found to be only partly soluble in good solvents after exposure to ultraviolet radiation at room temperature in vacuum or nitrogen. The solubility and swelling ratio results for irradiation in vacuum at room temperature are shown in Figures 3 and 4, respectively. Since both swelling ratio and gel content can be related to extent of crosslinking, it is expected that two curves will exhibit certain similarities. After a short period an insoluble fraction, presumably made up of crosslinked polymer, appears. As the time of irradiation is extended the insoluble fraction increases and becomes less swollen, indicating an increasing extent of crosslinking.

The data presented in Figure 5 indicate that on exposure to ultraviolet irradiation a part of the polymer remains soluble, and that with increasing time of irradiation, the intrinsic viscosity of the soluble portion decreases. This decrease in intrinsic viscosity can be explained by considering that the bond breaking reaction which precedes crosslinking also leads to reactions producing a polymer of lower molecular weight. Or, there may be another type of scission, a main-chain scission independent of the crosslinking mechanism, that causes the decrease in intrinsic viscosity.

The number of crosslinked units per initial primary weight-average molecule, δ, has been determined by Charlesby's method and tabulated in
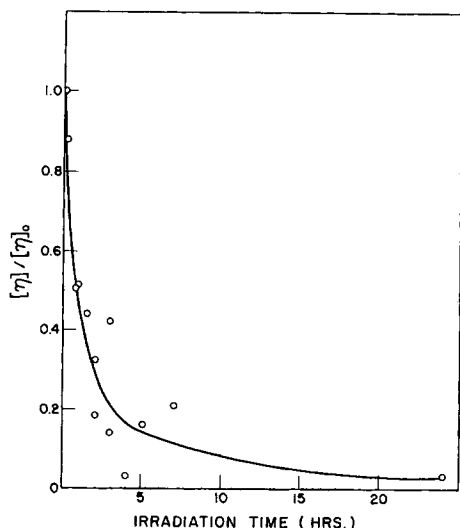
Fig. 5. Intrinsic viscosity of the soluble portion of irradiated poly(ethyl acrylate).

Fig. 6. Weight fraction solubles $(1 - g)$ vs. crosslinked units per initial primary weight-average molecule, δ, for poly(ethyl acrylate).

Table I. The results obtained from the theory will be shown to be in substantial agreement with the experimental facts, which suggests that the theoretical treatment of polymers crosslinked by ionizing irradiation is applicable to crosslinking caused by ultraviolet irradiation.

TABLE I

The Number of Crosslinked Units per Initial Primary Weight-Average Molecule, δ, from Solubility Data

Irradiation time, R, hr.	Poly(ethyl acrylate)	
	Soluble fraction $1 - g$	δ $\beta/\alpha = 0.50$ $R_0{}^* = 0.40$
0.25	1.000	0.62
0.50	a	1.2
1.0	0.550	2.5
1.5	0.418	3.8
2.0	0.342	5.0
3.0	0.278	7.5
5.0	0.209	12
7.0	0.187	18
16.0	0.102	40

a A slight amount of insoluble polymer was observed in this case but it could not be measured by the technique used.

The first point to note is that in Figure 6 the theoretical curve for an assumed value of β/α satisfactorily fits the experimental points. The value of $R_0{}^*$, the theoretical time to produce incipient gelation if no main-chain scissioning has occurred, is 0.4 hr. This can be compared with the experimental observations that at 0.25 hr. the polymer was completely soluble but at 0.5 hr. there
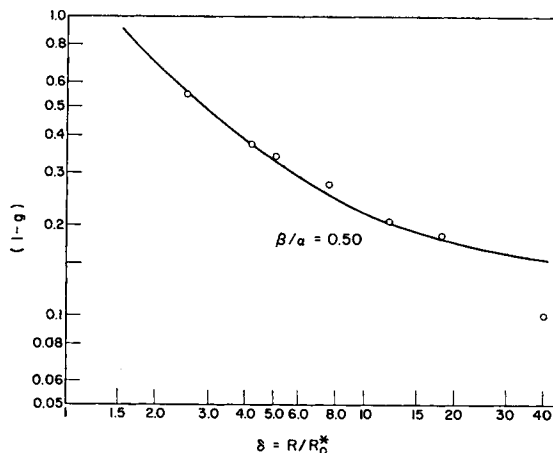
was a slight amount of insoluble polymer observed. At 0.25 hr., when the irradiated polymer was completely soluble, δ has a value of 0.62 corresponding to $\delta'' = 0.54$. According to the theory this is possible only before gelation, since incipient gelation occurs when there exists one crosslinked unit per weight-average molecule of the instantaneous primary distribution, $\delta'' = 1$.

In order to compare the Charlesby and Flory-Rehner theories the crosslink contents obtained must be calculated in the same terms. The equations below are used to convert gel content data to ν_e/V_0, the quantity calculated by the Flory-Rehner theory. The moles of crosslinked units per unit volume is given by:

$$\nu/V_0 = \delta''/(\bar{v}M'')$$

Then, using Flory's correction term to obtain ν_e, the effective moles of crosslinked units,

$$\nu_e = \nu(1 - 2M_c/M'')$$

substituting for M_c according to

$$M_c = M''/(\delta'' + 1)$$

and for M'' with

$$M'' = M(\delta''/\delta)$$

the final equation is obtained:

$$2\left[\frac{\delta\,(\delta'' - 1)}{\bar{v}M\,(\delta'' + 1)}\right] = \frac{\nu_e}{V_0}$$

The factor 2 was introduced because the left-hand side of the equation is a weight-average quantity. The molecular weight M was obtained from the initial intrinsic viscosity using the equation,[20]

$$[\eta] = 5.33 \times 10^{-3} P_n^{0.66}$$

and the specific volume, $\bar{v}$, was calculated from the density, reported as 1.12 g./cc.[21]
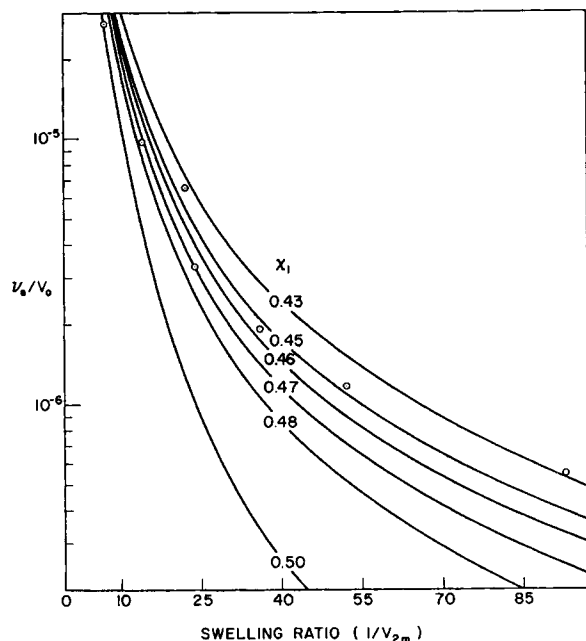

Fig. 7. Crosslink contents calculated from solubility vs. swelling ratios. Solid lines are theoretical swelling equation curves.

The values of (ν_e/V_0) calculated from the Flory-Rehner theory (swelling data) and from the Charlesby theory (gel content data) are given in Table II. Figure 7 contains curves of the theoreti-

TABLE II
Moles of Crosslinked Units per Unit Volume, ν_e/V_0, Calculated from Solubility Data

Irradiation time, hr.	Swelling ratio, $1/v_{2m}$	Swelling $\nu_e/V_0 \times 10^6$ $\chi_1 = 0.46$	Solubility $\nu_e/V_0 \times 10^6$
0.25	—	—	—
0.50	>93	—	—
1.0	93	0.40	0.57
1.5	52	0.91	1.18
2.0	36	1.8	1.91
3.0	24	3.9	3.33
5.0	22	4.7	6.53
7.0	14	14	9.59
16.0	6.9	56	27.1

cal swelling equation for different values of χ_1, and (ν_e/V_0) from gel content data is plotted against the experimental swelling ratios. The fact that a good fit for a constant value of χ_1 was not obtained
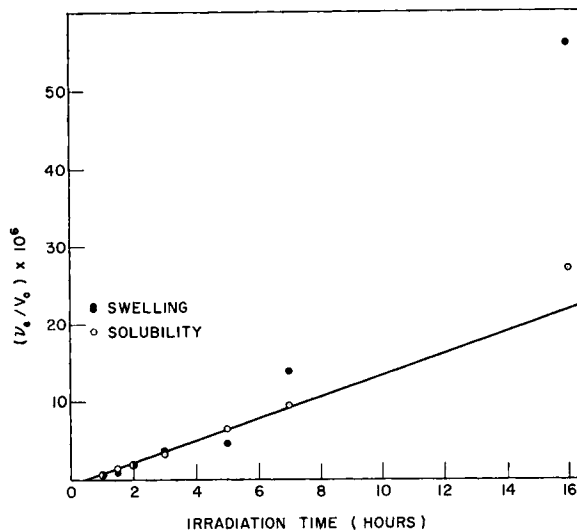

Fig. 8. Moles of crosslinked units per unit volume, ν_e/V_0, calculated from solubility and swelling data ($\chi_1 = 0.46$).

agrees with recently published results for other polar polymers in polar solvents,[22,23] where freezing point experiments showed that χ_1 varied with the volume fraction of polymer in solution. Our results suggest that a similar experiment with poly-(ethyl acrylate) in acetone will show χ_1 to vary with polymer concentration. The Charlesby and Flory-Rehner results are also compared in Figure 8 where (ν_e/V_0) is plotted against irradiation time. The filled circles are calculated from the swelling measurements and an average $\chi_1 = 0.46$. The open circles are (ν_e/V_0) calculated from the solubilities of the same samples. The agreement is best at fairly short irradiation times, corresponding to a relatively low degree of crosslinking, up to about 10^{-5} moles of crosslinked units/unit volume. We should expect to get better agreement at low degrees of crosslinking because complications due to entanglements and intramolecular crosslinking are not as significant as at higher levels.

Conclusions

Ultraviolet irradiation of poly(ethyl acrylate) films in vacuum causes simultaneous crosslinking and scission of the polymer chains. Charlesby's method for treating solubility data for polymers exposed to ionizing radiation appears to be applicable to poly(ethyl acrylate) irradiated with ultraviolet light. Crosslink data obtained from this method did not give a constant value for χ_1, the polymer solvent interaction parameter in the Flory-Rehner theory. Its value appeared to depend on the vol-

ume fraction of polymer in the swollen network. Crosslink contents calculated from swelling data by using an average value for χ_1 in the Flory-Rehner equation were in good agreement with the values from gel content data at values less than 10^{-5} moles of crosslinked units per cm.[3].

Mr. B. B. Kine very kindly prepared for use the poly(ethyl acrylate) used in this work.

References

1. Schultz, A. R., and F. A. Bovey, *J. Polymer Sci.*, **22**, 485 (1956).

2. Schultz, A. R., P. I. Roth, and G. B. Rathmann, *J. Polymer Sci.*, **22**, 495 (1956).

3. Ellis, C., and A. A. Wells, *The Chemical Action of Ultraviolet Rays*, revised and enlarged by F. F. Heyroth, Reinhold, New York, 1941, chapters 30–32.

4. Bovey, F. A., *The Effects of Ionizing Radiation on Natural and Synthetic High Polymers*, Interscience, New York, 1958.

5. Oster, G., G. K. Oster, and H. Moroson, *J. Polymer Sci.*, **34**, 671 (1959).

6. Oster, G., G. K. Oster, and H. Moroson, Abstracts of Papers, 132nd Meeting of the American Chemical Society, New York, September 8–13, 1957.

7. Cowley, P. R. E. J., and H. W. Melville, *Proc. Roy. Soc. (London)*, **A210**, 461 (1952).

8. Sobue, H., Y. Tabata, and Y. Tajima, *J. Polymer Sci.*, **27**, 596 (1958).

9. Winkler, D. E., *J. Polymer Sci.*, **35**, 3 (1959).

10. Reiney, M. J., M. Tyron, and B. G. Achhammer, *J. Research Natl. Bur. Standards*, **51**, 155 (1953).

11. Grassie, N., *Chemistry of High Polymer Degradation Processes*, Interscience, New York, 1956, chapter 4.

12. Naunton, W. J. S., *Trans. Faraday Soc.*, **38**, 332 (1942).

13. Bateman, L., *J. Polymer Sci.*, **2**, 1 (1947).

14. Stillings, R. A., and R. J. Van Nostrand, *J. Am. Chem. Soc.*, **66**, 753 (1944).

15. Lawton, T. S., and H. K. Nason, *Ind. Eng. Chem.*, **36**, 1128 (1944).

16. Flory, P. J., and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 512 (1943).

17. Charlesby, A., *Proc. Roy. Soc. (London)*, **A222**, 60, 542 (1954).

18. Hachihama, Y., and H. Sumitomo, *Tech. Repts. Osaka Univ.*, **3**, 385 (1953); *C. A.*, **49**, 698a (1955).

19. Hansen, J. E., M. G. McCarthy, and T. J. Dietz, *J. Polymer Sci.*, **7**, 77 (1951).

20. Hachihama, Y., and H. Sumitomo, *Tech. Repts. Osaka Univ.*, **5**, 485 (1955); *C. A.*, **51**, 8474a (1957).

21. Orofino, T. A., and J. A. Shetter, unpublished data, The Rohm & Haas Co.

22. Booth, G., G. Gee, and G. R. Williamson, *J. Polymer Sci.*, **23**, 3 (1957).

23. Kawai, T., *J. Polymer Sci.*, **32**, 425 (1958).

Synopsis

Films of poly(ethyl acrylate) were irradiated in a vacuum with ultraviolet light of 254 mμ wavelength, and changes in their swelling, solubility, and intrinsic viscosity were determined. The results were interpreted as being due to simultaneous crosslinking and chain scission. The ratio of the rates of the two processes was determined from solubility data by means of Charlesby's theory and it was found that two crosslinked units form for each chain scission. Crosslink contents obtained in this way and the swelling data were used to evaluate χ_1, the polymer-solvent interaction constant, in the Flory-Rehner theory. It was found that χ_1 was not a constant with the solvent used, which was acetone. However, using an average χ_1 of 0.46, which has also been reported from osmotic pressure data, crosslink contents calculated from the Flory-Rehner theory were in good agreement with those from solubility data for values less than 10^{-5} moles of crosslinked units per cm.[3].

Résumé

Des films de polyacrylate d'éthyle ont été irradiés dans le vide par la lumière ultraviolette à 254 mμ et on a déterminé les changements dans le point de fusion, la solubilité et la viscosité intrinsèque. Les résultats ont été interprétés comme étant dus à un pontage et à une scission de chaîne simultanément. Le rapport des vitesses des deux processus a été déterminé à partir des résultats de solubilité en employant la théorie de Charlesby et on a trouvé qu'il se forme deux unités pontées pour chaque scission de chaîne. Le nombre de ponts obtenu de cette manière et les résultats obtenus par fusion ont été utilisés pour évaluer χ_1, constante d'interaction polymère-solvant dans la théore de Flory-Rehner. On a trouvé que χ_1 n'était pas une constante avec le solvant utilisé, l'acétone. Cependant, en employant une moyenne de 0,46 pour χ_1, obtenue également à partir des résultats osmotiques, les nombres de ponts calculés d'après la théorie de Flory-Rehner sont en accord avec ceux obtenus à partir des résultats de solubilité pour des valeurs inférieures à 10^{-5} moles d'unités pontées par cm³.

Zusammenfassung

Filme aus Poly(äthylacrylat) wurden im Vakuum mit ultraviolettem Licht von der Wellenlänge 254 mμ bestrahlt und die Veränderung ihrer Quellung, Löslichkeit und Viskositätszahl bestimmt. Die Ergebnisse wurden als Wirkung einer gleichzeitigen Vernetzung und Kettenspaltung gedeutet. Das Verhältnis der Geschwindigkeiten der beiden Prozesse wurde aus Löslichkeitsdaten nach der Theorie von Charlesby bestimmt. Es wurd gefunden, dass auf jede Kettenspaltung zwei Vernetzungsstellen gebildet werden. Der auf diesem Wege erhaltene Gehalt an Vernetzungsstellen wurde gemeinsam mit den Quellungsdaten zur Ermittlung von χ_1, der Wechselwirkungskonstanten Polymer-Lösungsmittel in der Theorie von Flory-Rehner, verwendet. Es wurde gefunden, dass bei Aceton, das als Lösungsmittel verwendet wurde, χ_1 keine Konstante war. Bei Verwendung eines Mittelwertes von 0,46 für χ_1, der auch dem veröffentlichten osmotischen Wert entspricht, war jedoch der aus der Theorie von Flory-Rehner berechnete Gehalt an Vernetzungsstellen für Werte kleiner als 10^{-5} Mole Vernetzungsstellen pro cm³ in guter Übereinstimmung mit dem aus Löslichkeitsdaten berechneten.