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ON THE REGULARITIES OF RADIATION VULCANIZATION OF POLYAMIDES

(USING ANID G-669 AS AN EXAMPLE)

(Presented by Academician V. A. Kargin, 25 VI 1958)

As is known, according to the character of radiation-chemical transformations, two types of linear polymers can be distinguished: vulcanizing polymers and polymers undergoing degradation. Whether a given polymer belongs to one of these types is judged from the nature of changes in mechanical and thermomechanical properties, solubility, and solution viscosity, i.e., properties that make it possible to evaluate only the overall process of change in the molecular structure of the polymer. At the same time, in discussing the results of experimental studies, it is often assumed that, under the action of radiation in a linear polymer, both reactions of formation of cross-links and reactions of bond scission in the main chains of macromolecules proceed simultaneously, and that the observed overall process is determined by the predominance of one of these two reactions. The very fact that these oppositely directed reactions proceed simultaneously, as well as their relative rates, is judged only by indirect indications (1,2).

In the present work, the task was set of obtaining experimental evidence for the simultaneous occurrence of degradation and structuring reactions under the action of ionizing radiation on polyamides. As the object of study, the soluble mixed polyamide "anid G-669" was chosen, which is a product of polycondensation of hexamethylenediamine with adipic and azelaic acids and caprolactam (3). It had previously been established that the total effect of ionizing radiation on this polyamide (4), as well as on polyhexamethylene adipamide (4,5), amounts to radiation vulcanization.

Samples of polyamide G-669 in the form of plates 1 mm thick were irradiated both in air and in vacuum. An X-ray tube of the TRB-3 type (6), operating at a voltage of 80 kV and a current of 20 mA,* was used as the source. The dose rate was of the order of $5 \cdot 10^{16}$ eV/cm^3·sec., and the duration of irradiation was 1-20 hours.

Figure 1

Figure 1: Figure 1

Figure 1 presents thermomechanical compression curves of samples of anid G-669 as a function of dose. The curves shown, recorded by a continuous method using the apparatus described in (7), illustrate the general character of the overall process of radiation vulcanization. Similar results were obtained in studying the solubility of irradiated samples: already as a result of 3-hour irradiation, a fraction insoluble in acetic acid appears (7 wt.%), the amount of which increases with further increase in dose and amounts to 25% after 5 hours and 76% after 10 hours of irradiation.

* Irradiation of the samples was carried out on X-ray installations of the Institute of Physical Chemistry of the Academy of Sciences of the USSR. The authors express their gratitude to Prof. N. A. Bakh and V. I. Zatulovsky for providing the opportunity to carry out the work.

Determination of the weight-average molecular weight M_w of the polyamide by measuring light scattering in an ethanol solution showed that, under the action of radiation, it increases sharply: for the unirradiated sample $M_\mathrm{w} = 14500$, while already for a sample irradiated for 1 hour, $M_\mathrm{w} = 55000$.

Figure 2 presents curves of the dependence of the viscosity of solutions on concentration for anide G-669 in cresol and acetic acid. As a result of irradiation, the value $[\eta]$ for cresol solutions decreases, while for acetic-acid solutions it increases. At the same time, the slope of the concentration curves increases in both cases, which indicates an increase in the Huggins constant (8) in the equation:

$$\eta/C = [\eta] + k[\eta]^2 C.$$

Fig. 1. Thermomechanical shrinkage curves of anide G-669 as a function of dose (specific load 0.8 kg/cm^2)

Figures 3 and 4 present the results of turbidimetric titration of unirradiated and irradiated samples of anide G-669 in the form of integral and differential distribution curves with respect to solubility. The titration data given refer to a system in which acetic acid was used as the solvent and water as the precipitant. In the case of samples that received relatively large doses and contained an insoluble "gel fraction," the magnitude of the latter was determined independently and taken into account in constructing the integral distribution curves, by plotting the corresponding values on the ordinate axis (dashed lines in Fig. 3). It should be borne in mind that, for irradiated samples, the results obtained only approximately reflect the true molecular-weight distribution, since under the action of radiation the dependence of the polymer solubility on its molecular weight may change to a certain extent. However, these curves make it

Figure 2

Figure 2: Figure 2

possible to judge with sufficient certainty the general character of the change in the molecular-weight distribution. Examination of Fig. 4 shows that, as a result of irradiation, the maximum on the initial differential distribution curve splits: instead of one maximum, two appear, one of which is shifted into the region of high-molecular, poorly soluble fractions, and the other into the low-molecular region. As the dose is increased, these two maxima continue to "move apart." In the case of doses exceeding the gelation dose, the differential curves shown in Fig. 4 correspond to the distribution with respect to solubility within the sol fraction, owing to which the absolute

Fig. 2. Viscosity of solutions of unirradiated $(1, 3)$ and irradiated for 1 hour $(2, 4)$ samples of anide G-669. $1, 2$—solvent cresol; $3, 4$—solvent acetic acid.

the value of the "high-molecular maximum" decreases as the insoluble fraction increases.

The experimental data obtained show that, under the action of radiation in polyamide, both processes of formation of cross-links and processes of destruction of the main chains of macromolecules proceed simultaneously. The occurrence of structuring reactions is demonstrated by the facts of an increase in

[Figure 3]

Fig. 3. Integral distribution curves of anid G-669 samples by solubility as a function of dose

the value M_{B}, the shift of the maximum on the solubility distribution curves toward less soluble fractions and, finally, the appearance at sufficiently high doses of an insoluble three-dimensional fraction and loss of flow at the melting temperature of the original polymer. The simultaneous occurrence of destruction reactions of the main chains is indicated by the "splitting" of the differential distribution curves, i.e., the appearance on them of a second maximum in the region of relatively well-soluble fractions, which subsequently shifts continuously into the low-molecular region. As a result of the simultaneously proceeding processes of structuring and destruction, the initial polyamide with the usual relatively narrow distribution appears to break down into two independent fractions—low-molecular and high-molecular. This can be explained by the fact that, as a result of the interaction of primary polymer radicals, new molecules are formed whose size is either significantly greater (interaction of radicals with neighboring macromolecular chains), or significantly smaller (disproportionation and isomerization of radicals, their interaction with low-molecular particles) than the initial value. At the same time, in the case considered here, the structuring processes predominate, and the final result of the transformation is vulcanization. The amount and "density" of three-dimensional formations continuously increase with increasing dose, as is evident from the data of thermomechanical studies and solubili-

[Figure 4]

Fig. 4. Differential distribution curves of anid G-669 samples by solubility as a function of dose. 1 –unirradiated, 2 –irradiated for 1 hour, 3 –2 hours, 4 –5 hours, 5–10 hours.

dependence. Already at the first stages of the process the branching of the polymer molecules increases to a large extent, as follows from the character of the change in the viscosity of the solutions and, first of all, from the fact of the increase in the Huggins constant for solutions of irradiated samples.

The data presented show that a comprehensive investigation of changes in mechanical properties, as well as the properties of solutions, changes in molecular weights and in the molecular-weight distribution function makes it possible to assess, with sufficient completeness, changes in the molecular structure of polyamides in the course of their radiation-chemical transformations.

Apparently, the application of analogous methods of investigation will make it possible to separate the concurrently occurring reactions of structuring and degradation of polymers of different structure and to establish the factors affecting their relative rates.

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CITED LITERATURE

[1] B. L. Tsetlin, N. G. Zaitseva, V. A. Kargin, Report of the Institute of Physical Chemistry, Academy of Sciences of the USSR, No. 676 (April 1953); B. L. Tsetlin, N. G. Zaitseva, V. M. Korbut, V. A. Kargin, in: *The Action of Ionizing Radiations on Inorganic and Organic Systems*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 362.
[2] A. R. Schultz, P. J. Roth, G. B. Rathman, J. Polym. Sci., 22, No. 102, 495 (1956).
[3] V. V. Korshak, T. M. Frunze, Izv. AN SSSR, OKhN, 1957, 558.
[4] B. L. Tsetlin, S. R. Rafikov, Izv. AN SSSR, OKhN, 1957, 1411.
[5] A. Charlesby, Nature, 171, 167 (1953).
[6] V. I. Zatulovskii, N. I. Vitushkin, D. I. Naryadchikov, V. I. Petrovskii, Tr. 1st All-Union Conference on Radiation Chemistry, Publishing House of the Academy of Sciences of the USSR, 1958, p. 313.
[7] B. L. Tsetlin, V. I. Gavrilov, N. A. Velikovskaya, V. V. Kochkin, Zav. lab., No. 3, 352 (1956).
[8] M. Huggins, J. Am. Chem. Soc., 64, 2716 (1942).

Note: Figure translations are in progress. See original paper for figures.