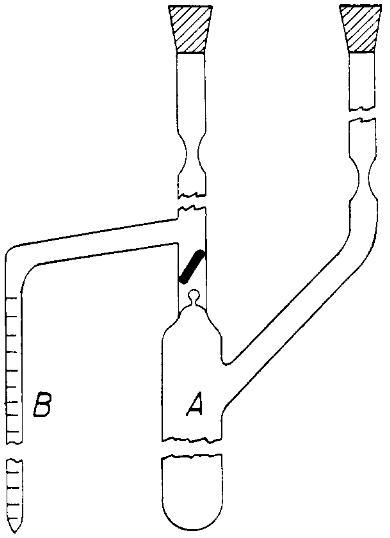

Figure 1. Vial for polymerizations in the presence of gaseous monomer.

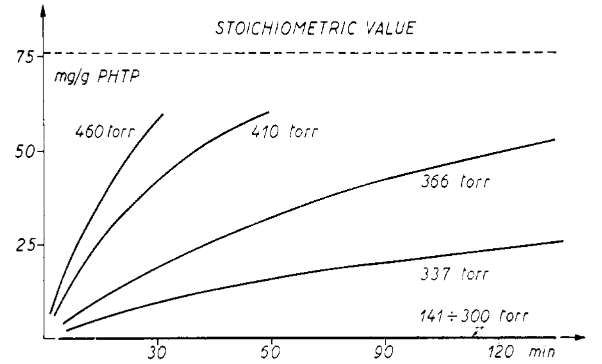

Figure 2. Absorption of *trans*-1,3-pentadiene in racemic nonirradiated PHTP; temperature of the crystal phase (t_A), 30°.

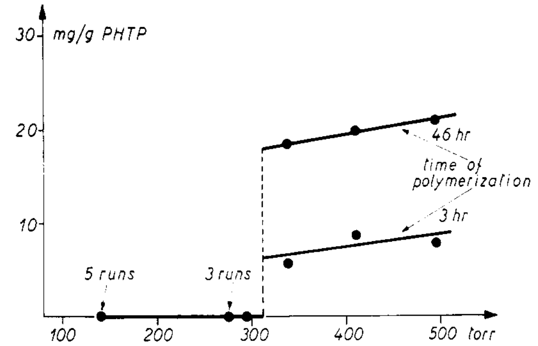

Figure 3. Dependence of the polymerization yield on monomer pressure; polymerization temperature (t_A), 30°.

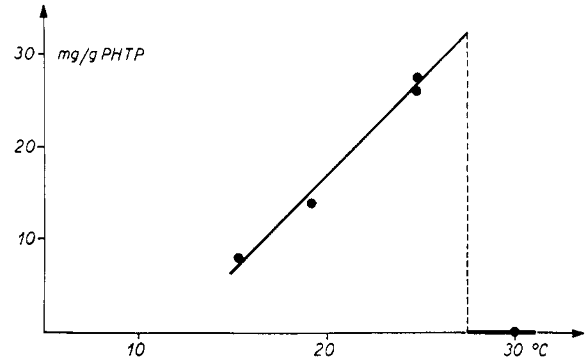

Figure 4. Dependence of the polymerization yield on temperature; monomer pressure, 275 Torr (t_B = 15.3°).

the pressure is higher than that of the saturated solution (*i.e.*, when $t_B \geqslant t_A$) an indefinite passage of the volatile component from B to A is observed.

The above data would supply decisive proof against our hypothesis only if the polymerization occurs at a pressure lower than that of decomposition of the adduct. However, our tests show that under such conditions the polymerization does not take place.

Figure 3 shows the dependence of the polymerization yield on pressure (t_B ranging between 15 and 30°), the radiation dose, time of aging of preirradiated PHTP, and polymerization temperature (t_A = 30°) being the same. Yield is practically null until pressure nears that of formation of the adduct; then by a slight variation of pressure, the yield suddenly reaches a considerable value and later increases more slowly with further increases of pressure. Under our conditions, the polymerization rate is far lower than that of inclusion (compare Figure 3 with Figure 2).

The variation of the polymerization yield with temperature at a constant pressure (t_B = 15°, t_A ranging from 15 to 30°) gives results perfectly consistent with the previous ones (Figure 4). The amount of polymer increases until the temperature of decomposition of the adduct (at the operating pressure), above which it suddenly falls to negligible values.

These data clearly show that the polymerization takes place only in the stability range of the crystalline adduct PHTP–pentadiene; when pressure falls below or temperature rises above the point of decomposition (respectively by operating at a given temperature or pressure) the inclusion compound disappears and the polymerization does not proceed. Therefore, also the polymerization in the presence of preirradiated PHTP must be considered as a true inclusion polymerization occurring in homogeneous phase inside the channels of the crystalline lattice.

In another set of runs, we wanted to check whether a heterogeneous mechanism, in which the inclusion compound formed at the very moment of polymerization, was possible under different experimental conditions, *e.g.*, in the presence of γ rays. Irradiation was therefore carried out in the presence of gaseous monomer at a pressure lower than that of decomposition: under such conditions, no polymerization took place. This is a further proof of the above reported conclusions.

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Increased Energy Deposition in a γ-Irradiated Polymer *via* a Metallic Microphase

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When a multiphase system is exposed to high-energy electromagnetic radiation, it is possible that a phase will receive a dose which differs from that which it would absorb when irradiated alone. An effect of this kind is expected to be greatest when the difference in electron density between the two phases is large and, therefore, it was sought by combining nickel and nylon (electron densities in the ratio 6) and exposing them to Co-60 γ rays (average photon energy 1.25 MeV). Each phase would generate Compton recoil electrons in proportion to its electron density, and the loci of the energy deposition from these electrons would depend on their range and on the distribution of the phases. Increased energy deposition in the nylon would be favored by distributions which minimize reabsorption of electrons generated in the nickel.

In the present work nickel particles of diameter 5 μ were distributed in a continuous matrix of nylon. An obviously unfavorable distribution, from the point of view of increasing energy deposition in the nylon, would be the case where all the nickel particles are clustered together. At the other extreme, a uniform distribution of the particles would be unfavorable because, even at moderate volume per cents of metal, the spacing between particles would be small relative to the range of the recoil electrons and this would result in a dosage in the two phases not very different from that obtained when each is irradiated alone (*cf.* ref 1). For example, for 5 vol % of nickel the centers of the particles would be separated by about 15 μ, which is small relative to the range of a Compton recoil electron of average energy (0.6 MeV), which would be about 3×10^2 μ in nickel and about 2×10^3 μ in nylon. Nevertheless, it should be possible to significantly increase the dosage in the nylon *via* lower energy recoil electrons by working with segregated distributions of nickel particles such as are described below.

A sample of nylon-66 powder (Zytel 101, du Pont) of particle diameter 5–100 μ was mixed with nickel powder (123 Nickel, International Nickel Co.) and compacted in a cylindrical die (diameter 1.5 cm, length 2 cm) for 10 min at room temperature under a pressure of 1000 Kg/cm^2. Compacts ranging in composition from 0 to 15% by volume were sealed in evacuated ampoules and exposed to Co-60 γ rays at a dose rate of 3 Mrad/hr. The samples were exposed to air several days after irradiation. The solubility of the nylon in trifluoroethanol was estimated gravimetrically with allowance made for the insoluble nickel. Samples (5–10 mg) were heated along with a reference material which increased in temperature at a rate of 20°K/min in a du Pont DTA apparatus (900 Thermal Analyzer). The melting point of the crystalline regions in the polymer was taken as the minimum in the chart plot of the temperature difference between the control and the sample. The important quantity from the present point of view is the difference in melting temperature between various samples, and this appeared to be rather insensitive to rate of heating.

The compacts prepared in the above way do not have sufficient mechanical strength to sustain a plane of polish. However, an increase in coalescence of the nylon particles was effected by postirradiation heating at about 525°K, just below the melting point, sufficient to allow metallographic examination. In the micrograph the particles of metal appear as white spots against a dark background due to the polymer (Figure 1). Because of the possibility of motion during the heat treatment it should not be supposed that this micrograph accurately represents the distribution of metallic particles in the samples as irradiated. Nevertheless, it will be seen that zones of polymer are devoid of metallic particles and, in fact, the sizes of these zones approximate the particle size distribution of the original powder sample of nylon. Therefore, it is concluded that the compacts include a segregated rather than a random distribution of metallic particles of nickel. Further general information about the preparation and properties of similar compacts may be found in ref 2 and 3.

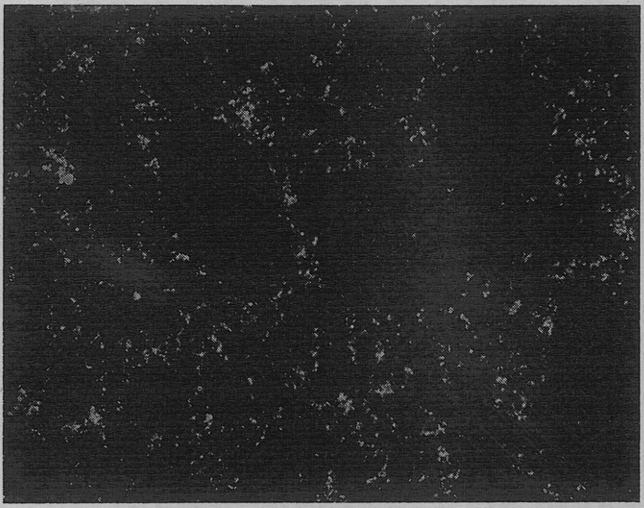

Figure 1. Photomicrograph showing 5%, by volume, of nickel (4–7 μ) in nylon (100×).

Evidence that the presence of nickel increased the energy deposition in nylon-66 on γ irradiation was provided by measurements of the gel content. After a dose of 64 Mrad, 28% of nylon was in the gel fraction and this was increased to 37% by inclusions of nickel in excess of 6% by volume. Precise measurements were difficult because of the presence of the nickel and, moreover, were judged to be unsatisfactory for providing a quantitative estimate of cross-linking, and hence, indirectly of energy deposition, because of the expectation that cross-linking density would be nonuniform in these experiments. Therefore, reference was made to the influence of nickel on depression of the melting point.

The DTA data in Table I show that an increase in the composition of nickel results in an increase in the depression of the melting point from the value T_0, for the unirradiated sample, to T_{64} after a dose of 64 Mrad [*cf.* $(T_0 - T_{64})$]. It will be seen that for the unirradiated samples inclusion of nickel has little or no influence on the melting temperature, T_0. By contrast, inclusion of nickel during irradiation continuously decreases T_{64}, almost doubling the depression at 15% by volume. A quantitative estimate of the damage may be obtained by use of eq 1, which relates the melting points T_{64} and T_0 to the mole fraction of units in the crystal, X, to the gas constant, R, of 2 cal mol^{-1} °K,$^{-1}$ and ΔH, the heat of fusion per mole of units.[4] The unit was taken to be $-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH-$ (gram molecular weight 226), for which the heat of fusion has been reported to be 1610 kcal/mol. The number of moles of units excluded from the crystal $(1 - X)$ was used to calculate a G value from eq 2 in which N_A is Avogadro's number, MW the molecular weight, D the dose in Mrad, and 6×10^{19} a conversion factor to correct this to electron volts per gram.

$$1/T_{64} - 1/T_0 = (-R/\Delta H) \ln X \qquad (1)$$

$$G(-\text{units}) = [(1 - X)N_A \times 10^2]/D(6 \times 10^{19})\text{MW} \qquad (2)$$

It is concluded that these data provide clear evidence that the presence of nickel does result in increased energy deposi-

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(3) R. P. Kusy and D. T. Turner, Preprints, AICLE Materials Engineering and Sciences Division, Atlanta, Ga., 1970, p 223.

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 568.

TABLE I: INFLUENCE OF NICKEL ON DEPRESSION OF THE MELTING POINT OF NYLON FOLLOWING γ IRRADIATION

% Ni	0			3			5			6			7			10			15		
DTA run	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
0 Mrad, T_0	539	537	537	539	537	537	539	537	536.5	539	537	537	540	537	537	541	538	537	540	539	538.5
64 Mrad, T_{64}	531.5	531	531	531.5	531	531	529.5	529	529	529	528.5	528.5	529	529	528.5	529	529	528.5	528	528.5	528.5
$T_0 - T_{64}$, °K	7.5	6	6	7.5	6	6	9.5	8	7.5	10	8.5	8.5	11	8	8.5	12	9	8.5	12	10.5	10
G(−units)	9	7.5	7.5	9	7.5	7.5	12	10	9	12	11	11	13	10	11	14	11	11	14	13	12

tion in the nylon. A further point of interest is that the method gives a G value of 7.5 in runs 2 and 3, which seems to provide a reasonable parallel with other estimates of chemical radiation damage; for example, *cf.* for nylon-66, G(free radicals) = 5.8.[5] Further commentary on the possibility of using this method as a convenient means of assessing chemical damage in crystalline polymers will be reserved pending completion of similar work on other polymers.

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[5] J. Zimmerman, *J. Appl. Polym. Sci.*, **2**, 181 (1959).

Communications to the Editor

Comments on a Recent Paper[1] by McIntyre and Campos-Lopez: "The Macrolattice of a Triblock Polymer"

In a recent paper,[1] McIntyre and Campos-Lopez describe the crystal structure of a polystyrene–polybutadiene–polystyrene block copolymer, determined by use of a low-angle X-ray diffraction technique. Having worked in the field of block copolymers since 1960, when it was first shown[2] that block copolymers are able to exhibit well-developed quasi-crystalline organizations, I would like to make a few comments on the arguments used and the conclusions drawn in this article. My purpose in doing so is not to give my own opinion about the real structure of the polymer under consideration: this would demand a complementary X-ray study of the sample in order to make sure first that the sample is composed solely of macrocrystals and not of the mixture of the organized phase with other separate phases, and second that the peaks registered[1] for diffraction angles smaller than 1000 sec truly correspond to the Bragg reflections of the macrolattice. My purpose in fact is merely to draw attention to some of the difficulties which are often encountered whenever a structural description of block copolymers is endeavored.

(i) These authors have recorded the low-angle X-ray diffraction diagram of their triblock copolymer; they have selected in this diagram several rather sharp peaks (*cf.* Table II[1]), and they have interpreted them as being due to the diffraction by a face-centered orthorhombic lattice characterized by the parameters $a = b = 676$ Å, $c = 566$ Å (*cf.* Figure 5[1]). However, if one calculates the Bragg spacings d_{hkl} of the diffraction lines of such a lattice—using the classical formula[3]

$$d_{hkl} = \left(\frac{h^2}{a_2} + \frac{k_2}{b_2} + \frac{l^2}{c^2}\right)^{-1/2}$$

holding for an orthorhombic lattice, and by substituting for the Miller indices h, k, l the correct values to take into account the fact that the lattice is face centered, *i.e.*, values which, depending upon the diffraction line under consideration, are all even or all odd—one finds that none of the observed peaks is in agreement with the expected ones. The misinterpretation of the experimental data is due to the fact that diffraction lines have been supposed to correspond to distances between structural elements in the crystal, instead of to distances between lattice planes (Bragg's law).

(ii) McIntyre, *et al.*, consider that, for diffraction angles larger than 1000 sec, where the intensity of the scattered X-rays is found to be low, the Bragg interferences fade off and, therefore, the scattering by an isolated structural element becomes apparent. Of course, this is in contradiction with the theory of X-ray diffraction by crystals. It is well known indeed[3] that the reflection of X-rays by a crystal occurs over a narrow angular range around the directions defined by Bragg's law and only around these directions, any departure from this behavior being merely due to disorder effects within the crystals.

(iii) They further consider that if the diffraction peaks do not lie too close to the zero-angle region, the radius of gyration of the structural elements may be determined from a Guinier plot. For the same reasons as those mentioned above, this is not possible: in the case of a crystal, even if it were of the type claimed by the authors, the Guinier plot gives valuable information, but only about the perfection and the extension in space of the crystal lattice.

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Received October 28, 1970

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[1] D. McIntyre and E. Campos-Lopez, *Macromolecules*, **3**, 322 (1970).

[2] A. Skoulios, G. Finaz, and J. Parrod, *C. R. Acad. Sci., Paris*, **251**, 739 (1960).

[3] A. Guinier, "X-Ray Crystallographic Technology," Hilger and Watts, Ltd., London, 1952, p 84.

The Effect of Pressure on the β-Relaxation of Polystyrene

The Tait equation relating volume and pressure has been shown to be applicable to amorphous polymeric systems, both in the liquid and glassy states.[1] The relation is frequently written in the form

$$1 - V/V_0 = C \ln (1 + P/B) \qquad (1)$$

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[1] V. S. Nanda and R. Simha, *J. Chem. Phys.*, **41**, 3870 (1964).