

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

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

damage in crystalline polymers will be reserved pending completion of similar work on other polymers.

Acknowledgments. We would like to thank the Division of Isotopes Development, U. S. Atomic Energy Commission, for its support of this work. For the use of the Co-60 source we are indebted to Dr. Leo Wall and the National Bureau of Standards.

Communications to the Editor

Comments on a Recent Paper¹ 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 shown² 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 registered¹ 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 II¹), and they have interpreted them as being due to the diffraction by a face-centered orthorhombic lattice characterized by the parameters $a = b = 676 \text{ \AA}$, $c = 566 \text{ \AA}$ (*cf.* Figure 5¹). However, if one calculates the Bragg spacings d_{hkl} of the diffraction lines of such a lattice—using the classical formula³

$$d_{hkl} = \left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right)^{-1/2}$$

holding for an orthorhombic lattice, and by substituting for the Miller indices h, k, l the correct values to take into account

(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 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 indeed³ 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

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

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

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