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.

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.

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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 quasicrystalline 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.

Antoine Skoulios
Centre de Recherches sur les Macromolécules, CNRS
Strasbourg, France
Received October 28, 1970

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

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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

$$1 - V/V_0 = C \ln (1 + P/B) \tag{1}$$

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

where V and V_0 are the volumes at pressures P and $P = 0$, respectively, and B and C are parameters. It could be established[1] that C is a universal constant having the same value of 0.0894 as for hydrocarbons.[2] The other adjustable parameter B is characteristic of the material and a function of temperature only. If the bulk modulus is defined as $K \equiv -V_0 \cdot (\partial P/\partial V)_T$, eq 1 yields a linear dependence on P, *viz.*

$$K = (B/C) + (P/C) \qquad (2)$$

When a transition occurs at a given temperature and pressure, the parameters of the Tait equation change and this can be readily noted by a "break" in the line. Wood[3] proposed to use this method to study transitions of polymers and successfully showed evidence of a rubber–glass transition of a vulcanized natural rubber in the results of Adams and Gibson,[4] although these authors found no indication of a transition in the analysis of their data.

We shall apply this method of analysis to polystyrene in a temperature region below the glass transition temperature. At atmospheric pressure, a relaxation region (β-relaxation) has been reported in the literature to occur anywhere between about 256 and 323°K, depending on the experimental method used, the nature of the sample and its thermal history.[5] Even the existence of a β-region has been disputed. The purpose of this note is to present evidence for, and the effect of pressure on, a subglass relaxation region in polystyrene.

We have designed and constructed an accurate high-pressure dilatometer using Bridgman's bellows technique. Mercury was chosen as the confining liquid. Calibration by means of benzene and mercury indicates an accuracy of $\pm 2 \times 10^{-4}$ cm^3/g in the measurement of specific volume change. A detailed description of the instrument will be given elsewhere.

The sample used was a thermally polymerized polystyrene (Dow Styron 686) with $M_w = 27.9 \times 10^4$ and $M_n = 9.7 \times 10^4$. It was studied at pressures up to 2 kbars and a temperature range between 7.7 and 75.4°. Since the PVT properties of a polymer glass depend strongly on its thermal history, the following uniform procedure was adopted. First, the polymer was heated to 130°, *i.e.*, 30° above its glass transition temperature; next it was cooled at a rate of 10°/hr to a reference temperature below the glass transition. The temperature was then held constant and the volume of the polymer measured as a function of pressure. Subsequently, the sample was again heated to 130° and cooled with the same specified rate to another temperature for another set of volume–pressure measurements.

A cryogenic dilatometer, similar in construction to that used previously,[6] was employed for length measurements, in this work between about −100 and +50° and at atmospheric pressure. The sample, in the form of a film, was cooled from about 120° to room temperature at a rate of 10°/hr, as in the pressure experiments, and then placed into the dilatometer where the required temperature range was scanned at a *heating* rate of 20°/hr.

Figure 1 is a plot of $-\Delta P/\Delta V$ *vs.* $\bar{P}$ for six temperatures, where ΔV is the volume change corresponding to a pressure change ΔP and $\bar{P}$ is the pressure at the midpoint of each pressure interval. Note that $\Delta P/\Delta V$ is related to the average bulk modulus $\bar{K}$ defined as $\bar{K} \equiv -V_0\Delta P/\Delta V$.

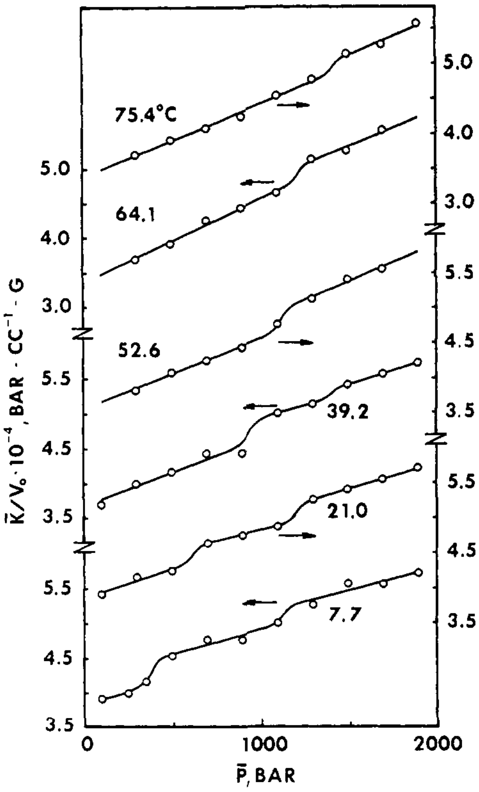

Figure 1. Ratio of mean bulk modulus $\bar{K}$, see text, and atmospheric pressure volume V_0, as a function of average pressure $\bar{P}$.

The linear portions of the curves are least-squares lines and are in accord with eq 2. The three highest temperatures show only one relaxation along each isotherm, whereas at the three lower temperatures there are indications of two relaxation regions. We consider here only the one at lower pressures, because of the limited information regarding the other. Two alternative procedures may be used to locate the transition pressure at a given temperature. One is based on the bulk modulus and determines graphically the inflection points of the S-shaped sections in Figure 1. The other is to compute the derivative of the compressibility $\kappa \equiv -(\partial \ln V/\partial P)_T$ by determining second derivatives of $\ln V$, using a moving arc procedure.[7] For this purpose we plot $\ln V$ *vs.* P on a large scale, draw a smooth curve through the experimental data, and then make use of additional points read off the curve. Seven-point, second-degree polynomials were used. The transition pressure is located as the minimum point on the curve of $(\partial\kappa/\partial P)_T$ *vs.* P and the result is shown in Figure 2. The use of two procedures should minimize the element of subjectiveness in establishing the existence and location of a transition pressure. Both yield essentially the same numbers, with a maximum difference of about 25 bars.

Figure 3 exhibits a plot of temperature *vs.* the corresponding transition pressure, as obtained by the differentiation method. The solid line represents a least-squares parabola, which would extrapolate to a β-relaxation temperature, T_β, of 261°K at atmospheric pressure. The slope of this curve obeys the relation

$$dT_\beta/dP = 4.80 \times 10^{-2} + 1.92 \times 10^{-5} \times P \qquad (3)$$

It is interesting to compare eq 3 with corresponding information regarding the glass transition temperature T_g. For the

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(2) W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, *J. Chem. Phys.*, **29**, 727 (1958); W. G. Cutler, Thesis, The Pennsylvania State University, 1955.

(3) L. A. Wood, *Polym. Lett.*, **2**, 703 (1964).

(4) L. H. Adams and R. E. Gibson, *J. Wash. Acad. Sci.*, **20**, 213 (1930); *Rubber Chem. Technol.*, **3**, 555 (1930).

(5) R. F. Boyer, see Table 3, Section Physical Properties—Dynamic Mechanical Loss Spectrum, in "Styrene Polymers," Encyclopedia of Polymer Science and Technology, N. Bikales, Ed., Interscience Publishers, New York, N. Y., in press.

(6) For example, R. A. Haldon and R. Simha, *J. Appl. Phys.*, **39**, 1890 (1968).

(7) J. L. Zakin, R. Simha, and H. C. Hershey, *J. Appl. Polym. Sci.*, **10**, 1455 (1966).

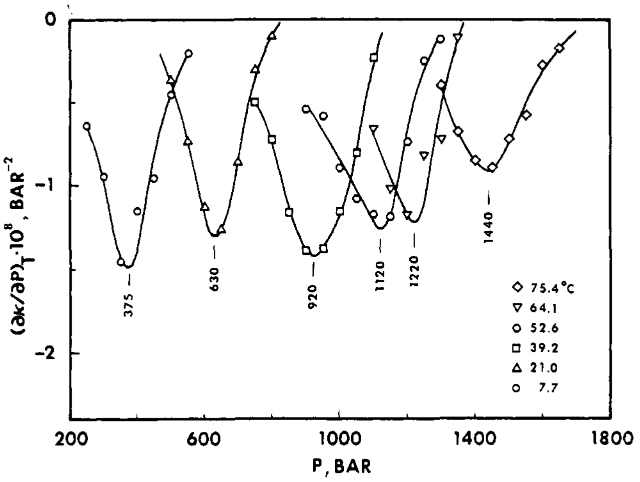

Figure 2. Pressure coefficient of compressibility κ as a function of pressure at a series of temperatures. Numbers at minima indicate transition pressures.

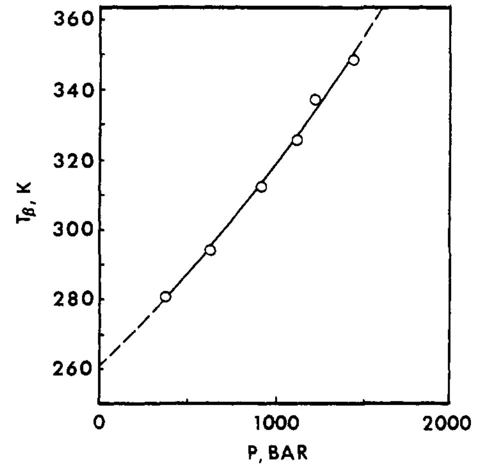

Figure 3. Relation between β-transition temperature and pressure. Points, experimental, obtained from Figure 2; solid line, least-squares equation (3); dashed portion, extrapolation.

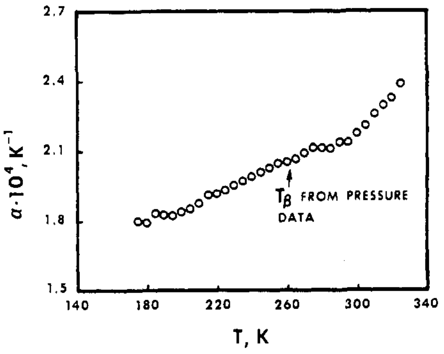

Figure 4. Thermal expansivity α as a function of temperature at atmospheric pressure. The arrow indicates the location of the temperature T_β from Figure 3.

same sample we obtain $dT_g/dP = 3.16 \times 10^{-2}$ deg bar^{-1} for $1 \leq p \leq 1750$ bars, in very good accord with published data. However, this result applies to the glass formed by *pressurizing* the liquid along a given isotherm. This state of the glass is not identical with that achieved by *cooling* the liquid below T_g at atmospheric pressure, as described in the experimental section. For a meaningful comparison we require the numerical value of dT_g/dP for the identical glass. We can estimate this quantity by extrapolating the isobars of the glass to intersect with the corresponding liquid isobars. This procedure yields

$$\lim_{P \to 0} dT_g/dP \cong 7.9 \times 10^{-2} \text{ deg bar}^{-1}$$

When analyzed in this manner, T_g is actually more sensitive to pressure than T_β and thus pressure will tend to resolve the two relaxation regions.

We have sought independent evidence for a β-relaxation region by means of thermal expansion measurements on an identical polymer sample. Figure 4 represents the thermal expansivity $\alpha \equiv (\partial \ln V/\partial T)_P$, derived from length measurements, and evaluated by the moving arc procedure[7] as a function of temperature at atmospheric pressure between 175 and 325°K. A broad relaxation region extending, say, between about 200 and 270°K will be noted. We may compare these results with two previous observations on the polystyrene system,[7,8] which encompass our temperature range. The numerical values are more or less the same and there is an increase in α corresponding to the upswing above 200°K in Figure 4. However, this increase appears to be less pronounced in the earlier work.

It is pertinent in this connection to mention infrared absorption measurements on a similar, although not identical styrene polymer. The derivative of the integrated band intensity at a wave number of 841 cm^{-1} exhibits a sharp decrease between 200 and 260°K.[9]

Finally, one may use the foregoing results to obtain rough estimates of the change ΔC_p in the heat capacity which may accompany the changes in α and κ in the β-relaxation process. We estimate from our measurements $\Delta\alpha = 0.30 \times 10^{-4}$ deg^{-1} and $\Delta\kappa = 0.28_4 \times 10^{-5}$ bar^{-1}. The various single ordering parameter relations then yield by means of eq 3 ΔC_p values of the order of 10^{-2} to 10^{-3} cal g^{-1} deg^{-1}. Such magnitudes should be observable, but the experimental situation does not seem to be clear. However, a value of 1 cal deg^{-1} mol^{-1} repeating unit has been reported for a relaxation process extending from 230 to 350 °K.[10]

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Anh Quach and Robert Simha
Division of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106
Received December 8, 1970

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