Dynamic X-Ray Diffraction Technique for Measuring the Crystal Lattice Response in Semicrystalline Polymers against Mechanical Excitations*

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Dynamic mechanical and crystallographic features which are associated with mechanical excitations on the bulk specimen of the semicrystalline polymers are generalized on the basis of factors such as mechanical dispersions of orientation of crystallites and deformation of the crystal superstructure. The latter factor may further be divided into inter-lamellae and intra-lamella responses within the superstructure such as spherulite.

The present paper describes the theory and techniques set up to observe the intra-lamella response in the semicrystalline polymers against mechanical excitations by means of a dynamic x-ray diffraction technique. This observation is required to measure the in-phase and out-of-phase components of the angular vibration of the diffraction maximum raised by the forced sinusoidal strain of the test specimen. For this purpose, it was shown that a twin detector technique could successfully be applicable where the diffraction peak shift was amplified by simultaneous measurements of the shoulder intensities of the diffraction perk at the higher and the lower diffraction angles to the peak maximum.

Introduction

Numerous studies have been made of the effects of dynamic mechanical excitations over wide ranges of frequency and temperature on the rheological behavior of the crystalline polymers in the bulk-crystallized as well as the solution-grown states. As a result of these, it has been found that there exists a characteristic mechanical dispersion, the so-called crystalline dispersion, at the leathery consistency of these materials. The dispersion consists of, at least, two types of dispersions designated as α_1 and α_2, which must arise from different types of crystalline relaxations associated with grain-boundary phenomena of crystallites dispersed within a medium of amorphous phase and with the crystal disordering transition, respectively.[1]

Recent investigations on the rheo-optical properties of low density polyethylene, by means of dynamic x-ray diffraction[2] and dynamic light scattering[3] techniques, have explained the crystalline relaxation mechanisms in terms of the temperature and frequency dispersions of orientation of crystallites[4-6] and deformation of the crystal superstructure (spherulite).[7,8] That is, the spherulite deformation, which is alomst instantaneous, is associated with the following two mechanisms; untwisting of crystal lamellae around their axes and tilting of molecular axes within the lamellae.[9,10] The former mechanism appears primarily at temperatures lower than the crystal disordering temperature of about 75°C for this polymer with an activation energy of 24 Kcal/mole,[4] whereas the latter appears at temperatures higher than the crystal disordering temperature with an activation energy of the order of 40 Kcal/mole.[6] The former mechanism must be assigned as the α_1 mechanism, the grain-boundary phenomena, arising from the orientation and/ or deformation of (elastic) crystal lamellae within the (viscous) medium of the amorphous phase, and the latter mechanism must correspond to the α_2 mechanism associated with the deformation of (viscoelastic) crystal lamellae due to the onset of torsional oscillation of polymer chains within the crystal lattice.[11]

Undoubtedly, the above explanations can better be reinforced if more detailed information about the dynamic responses, i.e., inter-lamellae and intra-lamella responses, can be obtained from some definite experimental sources. In this paper, a particular experimental technique to investigate the dynamic response, especially for the intra-lamella response in relation to the α_2 mechanism, will be proposed. The technique is a combination of the dynamic x-ray diffraction technique[2] with a twin detector technique for enabling the measurements of dynamic shift of x-ray diffraction peak from a given crystal plane along the Bragg angle, i.e., the dynamic lattice spacing response in the crystalline region of the semicrystalline polymers in the solid state.

Principle of Dynamic X-Ray Diffraction Technique

In the dynamic x-ray diffraction technique, the specimen is subjected to a sinusoidal strain given by

$$\lambda(t) = \lambda_0 + \Delta\lambda e^{i\omega t} \tag{1}$$

where λ_0 is the static strain which is necessary to hold the specimen taut during the vibration when the specimen is given as a long column or a thin film in its shape and is subjected to a tensile deformation, $\Delta\lambda$ the amplitude of the dynamic strain, and ω the angular frequency of the strain. On the other hand, the angular intensity distribution, $I(2\theta)$, of an x-ray diffraction peak can usually be approximated by either of Lorentz or Gaussian distribution function if the maximum intensity, I_m, the diffraction angle giving the maximum intensity, $2\theta_B$, and the an-

gular width at half-maximum intensity, β, of the diffraction peak are known.[11]
This can be expressed as

$$I(2\theta) = cI_m \tag{2}$$

where c is dependent on 2θ as given by

$$c = \chi[(2\theta - 2\theta_B)/\beta] = \chi(u), \tag{3}$$

$$u = (2\theta - 2\theta_B)/\beta. \tag{4}$$

In the above equation, χ is a function of u which gives the best agreement between
calculated [according to Eq. (2)] and observed diffraction intensity curves. It
must have, as typically seen in the Lorentz or Gaussian function, a symmetric
character as expressed by

$$\chi(u) = \chi(-u) \tag{5}$$

Now, it is assumed that the sinusoidal strain of the specimen represented
by Eq. (1) causes *also* sinusoidal variations of I_m as well as $2\theta_B$ of the diffraction
peak, while β is kept constant. Each of variations of I_m, $2\theta_B$ and β has, of course,
physical meanings. The sinusoidal variation of I_m means a sinusoidal change of
the number of crystallites per unit volume which take the proper orientation to
reflect the x-ray beam. The assumption of the constancy of β means that the
size distribution of the crystallites and the number of the defects within crystal-
lites does not change appreciably during the periodic small deformation of the
specimen and this perhaps approximates the real situation. The sinusoidal vari-
ation of $2\theta_B$ is the main topic to be discussed in this paper and will be explained
below in detail in terms of ε representing the tensile strain of lattice spacing.

Now, for the jth diffraction peak, the above assumption of sinusoidal vari-
ations of I_m and $2\theta_B$ can be expressed by

$$I_{m,j} = I^\circ_{m,j} + (\Delta I'_{m,j} + i\Delta I''_{m,j})e^{i\omega t} \tag{6}$$

$$2\theta_{B,j} = 2\vartheta^\circ_{B,j} + (\Delta 2\theta'_{B,j} + i\Delta 2\theta''_{B,j})e^{i\omega t} \tag{7}$$

where $\Delta I'_{m,j}$ and $\Delta I''_{m,j}$ are the in-phase and the out-of-phase components of the
variation of $I_{m,j}$, and $\Delta 2\theta'_{B,j}$ and $\Delta 2\theta''_{B,j}$ are the in-phase and the out-of-phase com-
ponents of the variation of $2\theta_{B,j}$ respectively. The superscription $^\circ$ represents
respective values at the static strain λ_0.

Let ε_j' and ε_j'' denote the in-phase and the out-of-phase components of the
dynamic tensile strain of the jth interplanar lattice spacing, then, by differentiat-
ing the Bragg equation with respect to θ, one has

$$\varepsilon_j' = \left(\frac{\Delta d_j}{d_j}\right)' = -\frac{1}{2}\cot\theta^\circ_{B,j} \cdot \Delta 2\theta'_{B,j} \tag{8}$$

$$\varepsilon_j'' = \left(\frac{\Delta d_j}{d_j}\right)'' = -\frac{1}{2}\cot\theta^\circ_{B,j} \cdot \Delta 2\theta''_{B,j} \tag{9}$$

where d_j is the distance of the interplanar spacing of the jth lattice plane giving
diffraction peak at $2\theta^\circ_{B,j}$, twice the Bragg angle $\theta^\circ_{B,j}$, and ε_j' and ε_j'' are the quan-

tities to be obtained in this study.

In practice, at an arbitrary diffraction angle $2\theta_i$, there usually appears an overlapping of contributions from several diffraction peaks. If the overlapping is additive, this situation can be represented by

$$I_i^\bullet = \sum_{j=1}^{N} c_{ij} I^\circ_{m,j} \tag{10}$$

where c_{ij} is given by

$$c_{ij} = \chi[2\theta_i - 2\theta^\circ_{B,j})/\beta_j^\bullet] = \chi(u), \tag{11}$$

$$u = (2\theta_i - 2\theta^\circ_{B,j})/\beta_j^\bullet. \tag{12}$$

In the dynamic situation, it can be shown that the diffracted intensity I_i observed at $2\theta_i$ exhibits sinusoidal variation on the basis of the sinusoidal variations of the maximum intensity and the diffraction angle as assumed in Eqs. (6) and (7) for each constituent diffraction peak.[2] The results are expressed as follows:

$$I_i = I_i^\bullet + (\Delta I_i' + i\Delta I_i'')e^{i\omega t} \tag{13}$$

where $I_i^\bullet$ is the same quantity as that appeared above in Eq. (10) and

$$\Delta I_i' = \sum_{j=1}^{N} (c_{ij}\Delta I'_{m,j} + k_{ij} I^\circ_{m,j}\Delta 2\theta'_{B,j}), \tag{14}$$

$$\Delta I_i'' = \sum_{j=1}^{N} (c_{ij}\Delta I''_{m,j} + k_{ij} I^\circ_{m,j}\Delta 2\theta''_{B,j}), \tag{15}$$

while k_{ij} is given by

$$k_{ij} = -(1/\beta_j^\bullet)(\partial\chi/\partial u). \tag{16}$$

$\Delta I_i'$ and $\Delta I_i''$, appearing on the left-hand sides of Eqs. (14) and (15), are the observable quantities by using a sector technique which is combined with photoelectric switches to activate and deactivate counting scalers in synchronization with the external strain phase of the specimen.[2] The values $I^\circ_{m,j}$, $2\theta^\circ_{B,j}$, $\beta_j^\bullet$, and $I_i^\bullet$ and the form of the function χ can be determined from the static measurement for the diffraction intensity curve of the specimen at the static strain λ_0 and from subsequent suitable corrections and resolutions of the overlapping peaks. Now, if two independent measurements for both $\Delta I_i'$ and $\Delta I_i''$ at two different diffraction angles are made for each of the N peaks, it is seen that $\Delta I'_{m,j}$ and $\Delta 2\theta'_{B,j}$, or $\Delta I''_{m,j}$ and $\Delta 2\theta''_{B,j}$, can be obtained by solving the simultaneous equations represented by Eqs. (14) and (15). This gives the theoretical basis for the dynamic x-ray diffractometer technique, in which the determination of $\Delta I'_{m,j}$ and $\Delta I''_{m,j}$ has been mainly discussed in the previous paper for measuring the dynamic orientation of crystallites in relation to the α_1 mechanisms.[2,4]

Application of Twin Detector Technique to Dynamic X-Ray Diffraction
Principle

Consider the case where a single diffraction peak is isolated from overlapping

with other peaks. Let's number this peak as j=1. For this peak, if measurements of $\Delta I_i'$ and $\Delta I_i''$ are made at $2\theta_1 = 2\theta^\circ_{B,1} + \gamma$ and $2\theta_2 = 2\theta^\circ_{B,1} - \gamma$, the following simple relations may be obtained:

$$c_{11} = c_{21} \tag{17}$$

$$k_{11} = -k_{21}. \tag{18}$$

In the above relations, it is advantageous to take γ to be a value so that the slopes of the peak become most steep at $2\theta_1$ and $2\theta_2$. From Eqs. (14), (15), (17) and (18), the following relations can readily be obtained:

$$\Delta I'_{m,1} = (\Delta I_1' + \Delta I_2')/(2c_{11}) \tag{19}$$

$$\Delta I''_{m,1} = (\Delta I_1'' + \Delta I_2'')/(2c_{11}) \tag{20}$$

$$\Delta 2\theta'_{B,1} = (\Delta I_1' - \Delta I_2')/(2k_{11}I^\circ_{m,1}) \tag{21}$$

$$\Delta 2\theta''_{B,1} = (\Delta I_1'' - \Delta I_2'')/(2k_{11}I^\circ_{m,1}). \tag{22}$$

Thus, the principle of the twin detector technique can best be applied in the above case. Practically, it can be applied with not so much error to a diffraction peak having negligibly small contributions of intensity from other peaks. These cases of isolated or nearly isolated diffraction peaks are often demonstrated by the reflections from the basal plane in the oriented specimen of crystalline polymers.

In a more general case where there exists considerable overlapping of diffraction peaks, the twin detector technique is also applicable, but in the sense that the twin detector technique facilitates the measurements with a faster speed. Recall that, as previously described, two independent measurements at two different diffraction angles for each of the diffraction peaks are necessary to obtain $\Delta 2\theta'_{B,j}$, $\Delta 2\theta''_{B,j}$, etc.

Construction and Design of a Twin Detector of New Type

The disadvantage of the twin detector technique is in the difficulties of producing a twin counter tube which shows with respect to the two constituent tubes strictly the same counting rate at various intensities of the x-ray quanta. In this study, this disadvantage was successfully overcome by using a single scintillation counter tube modified as the twin detector, instead of combining two tubes into a twin as employed in the usual twin detector technique. The basic design for this modification is to put a twin slit in front of the window (17×22 mm. NaI) of the scintillation counter. The constituent slits of this twin slit work alternately by shutters under a strict synchronization to the phase of external sinusoidal strain of the specimen. Such vibrational alternative operation of the slit is required to assure the simultaneity of measurement at diffraction angles corresponding to the two constituent slits which is the essential feature of the twin detector technique.

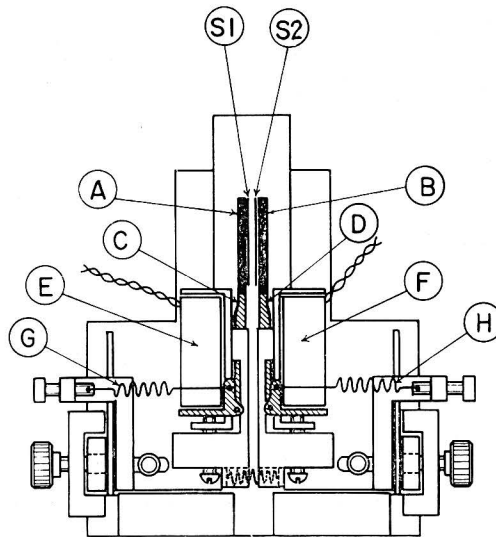Fig. 1 shows a schematic diagram of the twin slit. Each of the two slits (S1,

Fig. 1. Schematic diagram of the twin slit for the use of the dynamic x-ray diffractometer (*front*).
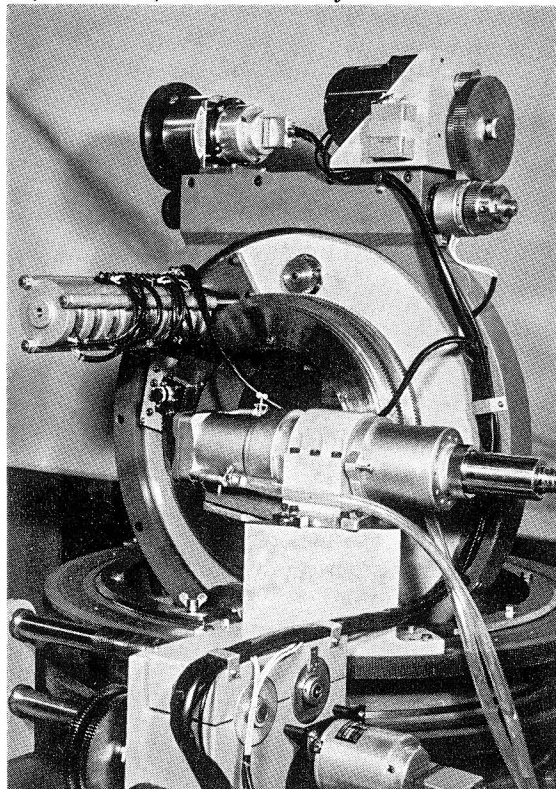

Fig. 2. On the vertical disk of the goniometer of the dynamic x-ray diffractometer, the four pairs of the photoswitches are arranged in parallel with fine phase-adjustable screws and are driven by a long common shaft which rotates in synchronization with the sinusoidal strain phase of the specimen.

S2), having a width of 0.20 mm., has a shutter (A, B) and the two shutters work alternately with equal time interval by the solenoid-driven shutter bars (C, D) seen in the figure as parts shadowed with hatching. When the current does not flow through the solenoid (E, F), the shutter bar, being pulled by the spring (G, H), drives the shutter outwards to open the slit. When the current flows, the solenoid attracts the amature of the shutter bar to drive the shutter inwards, and the slit is closed.

In the sector technique for the dynamic x-ray diffraction measurements,[2] it has been equipped with four sets of scaler, each of which is activated or deactivated by means of a pair of photoswitches at given phase angles of the sinusoidal strain of the specimen so that each scaler can count the diffracted x-ray intensity during the particular phase interval of the sinusoidal strain. Fig. 2 shows the photoswitches in operation. When one fixes the phase interval for every scaler as π radian and shifts the respective phase intervals with each other by $\pi/2$ radian, which is called as "π sector technique", the quantities, $\Delta I_i'$ and $\Delta I_i''$, can be obtained from the following relations:

$$I_i(0 \sim \pi) = I_i^\circ - (2/\pi) \Delta I_i'' \tag{23}$$

$$I_i(\pi \sim 2\pi) = I_i^\circ + (2/\pi) \Delta I_i'' \tag{24}$$

$$I_i(\pi/2 \sim 3\pi/2) = I_i^\circ - (2/\pi) \Delta I_i' \tag{25}$$

$$I_j(-\pi/2 \sim \pi/2) = I_i^\circ + (2/\pi) \Delta I_i' \tag{26}$$

where I_i $(0 \sim \pi)$, for example, means the integrated intensity of the x-ray diffraction at $2\theta_i$ during the phase interval between the phase angles 0 and π with respect to the sinusoidal strain of the specimen. In practice, however, each of I_i must be accumulated for sufficient cycles of the sinusoidal strain so as to avoid the statistical fluctuation of the x-ray quanta.

In order to simultaneously fulfill two independent measurements for $\Delta I_i'$ and $\Delta I_i''$ at two different diffraction angles, $2\theta_1$ and $2\theta_2$, both the two pairs out of the four scalers are required to be activated to count in the predetermined phase intervals of the sinusoidal strain of the specimen; i.e., for example, I_1 $(0 \sim \pi)$, I_1 $(\pi/2 \sim 3\pi/2)$, I_2 $(0 \sim \pi)$, and I_2 $(\pi/2 \sim 3\pi/2)$, provided that I_1° and I_2° are obtained from other sources of experiments, such as the static measurements at λ_0 or individual dynamic measurements at $2\theta_1$ and $2\theta_2$ using Eqs. (23) through (26). So it is seen that during the phase interval between $3\pi/2$ and 2π all of the four scalers are in the dummy state. This is shown schematically in Fig. 3. The time interval under the dummy state is the latitude time for the shutter to work and estimated to be $1/160$ second if the upper limiting vibration frequency, 40 Hz, of the dynamic x-ray diffractometer is allowed. Actually, the shutter works within a time interval of less than 1 msec. which corresponds to a sixth of the latitude
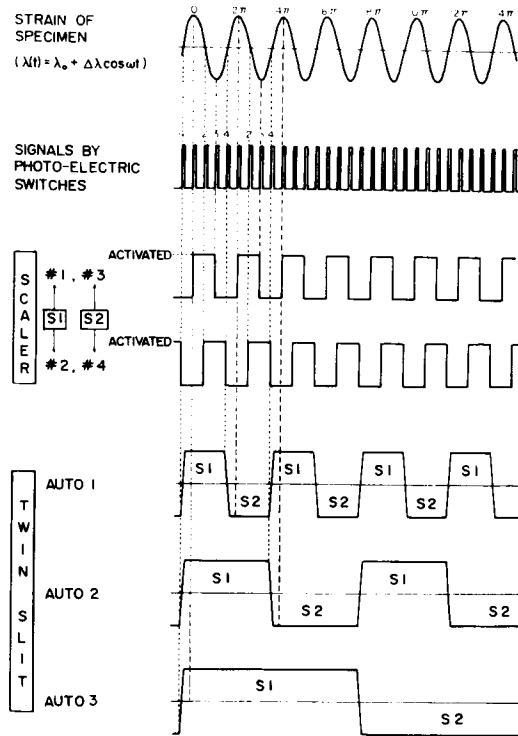
Fig. 3. Schematic diagram showing the relation between the
dummy phase intervals of the strain and the alternation
in the operation of the twin slit.

time estimated for the upper limiting frequency. As is shown in Fig. 3, the system is designed so that the shutter can work during the three choices of every, or every two, or every four dummy phase intervals. Thus, the net working time of each scaler is seen to amount to a quarter of the total time of observation when the π-sector technique is used.

Results of Construction

Fig. 4 shows the goniometer of the dynamic x-ray diffractometer to be equipped with the scintillation counter as modified to the twin detector by attaching the twin slit developed, and Fig. 5 shows the construction of the modified scintillation counter and the twin detector in detail. When the twin slit is removed and a single slit is attached, the counter can readily be converted to a usual single counter. The width between two constituent slits of the twin slit can be varied in five steps at present, i.e., 0.5, 0.75, 1.0, 1.25, and 1.5° in the angle of the 2θ. Fig. 6 shows the block diagram for operations of the twin slit and Table 1 shows some results. As seen in Table 1, the twin detector system developed in this study
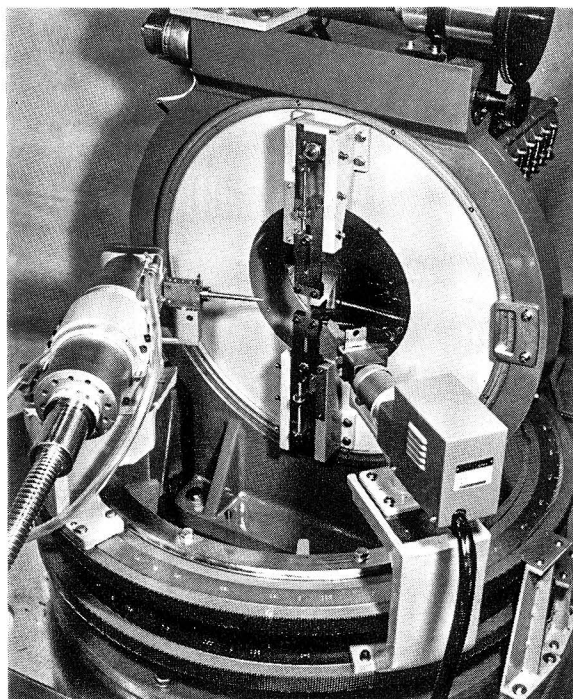
Fig. 4. Another view of the goniometer showing the x-ray tube and the scintillation counter fixed for the reflection technique. The scintillation counter is here used as a single detector.
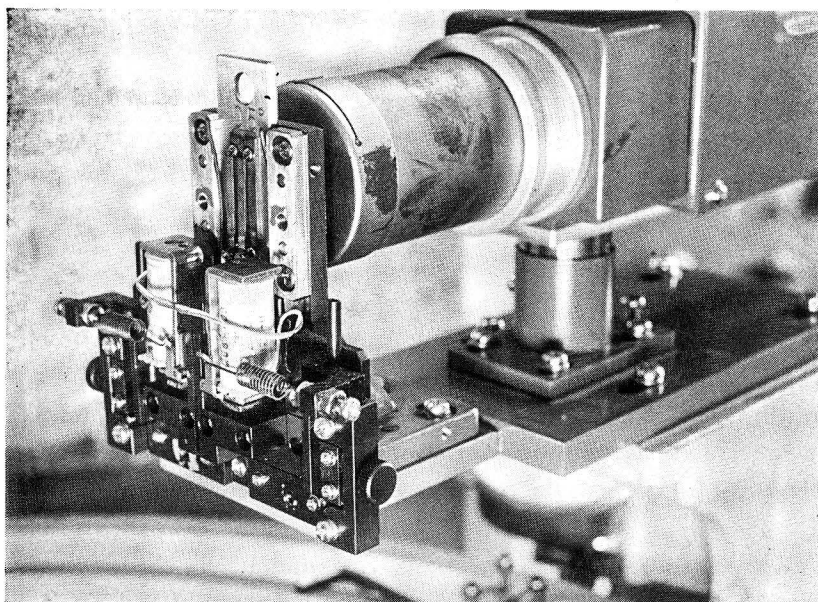

Fig. 5. Photograph showing the scintillation counter as modified to the twin detector by the twin slit.
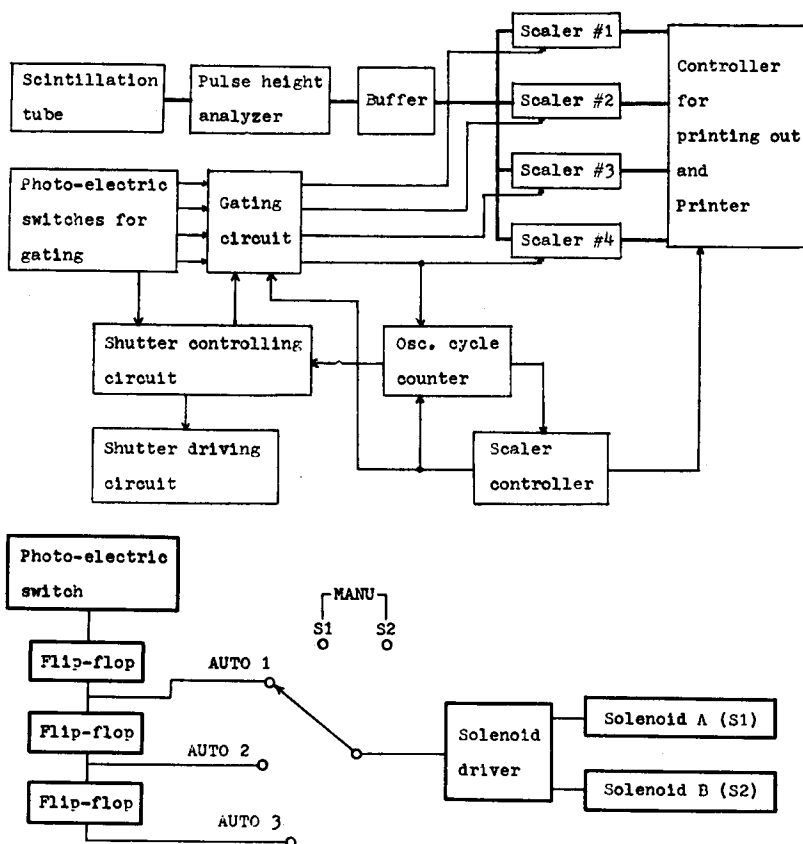
Fig. 6. Block diagram for operations of the twin slit.

Table 1. Results of the Use of the 1.0° Twin Slit*

Frequency (Hz)	Total Cycles of Vibration	Slit A		Slit B		$\dfrac{\text{(Intensity) Slit B}}{\text{(Intensity) Slit A}}$
		Accumulated Counts**	Intensity (c.p.s.)	Accumulated Counts**	Intensity (c.p.s.)	
0.01	10	624990	2488	645460	2569	1.0326
0.1	100	626290	2493	643960	2563	1.0281
1	1000	624780	2487	643160	2560	1.0294
10	10000	625980	2491	644320	2564	1.0293
			2490±3		2564±5	

* The 110 diffraction peak of high density polyethylene was measured with copper Kα radiation (40 kV and 18 mA). The gears to vibrate the specimen holding clamps were unlocked. The scintillation counter was fixed so that the x-ray quanta measured in the static situation by slit A and slit B, located respectively, at lower and higher angles to the intensity maximum, were almost equally balanced. Every dummy interval of the scalers was used for the operations of the twin shutters (see Fig. 3).

** Mean of the results by the two scalers.

shows almost no frequency dependence and gives sufficient accuracy for our purpose.

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