Investigation of Non-Ideal Two-Phase Polymer Structures by Small-Angle X-ray Scattering

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(Received 27 July 1972; accepted 10 October 1972)

The mean square of the electron-density gradient, $\langle |\text{grad}\, \eta|^2 \rangle$ in isotropic structures is shown to be proportional to the fourth moment of the SAXS intensity distribution in reciprocal space \( \int s^4 I(s) ds \), as well as to the second derivative of the correlation function in the origin. In the case of two-phase structures with unsharp phase boundaries, these relations may be used to find the thickness \( E \) of the transition regions. As was shown by Ruland [J. Appl. Cryst. (1971). 4, 70-73] \( E \) can also be determined by analysis of the intensity in the tail of the SAXS pattern. This approach is used here to investigate the effect of \( E \) on the one-dimensional correlation function. In the application of both methods, separation of the SAXS intensity from the continuous background of liquid scattering constitutes a critical step. A procedure in which the background is represented by a curve of the type \( a + bs^n \), where \( n \) is an even number, is found to work well for a number of polymers.

Introduction

In the investigation of two-phase structures by means of small-angle X-ray scattering (SAXS), the relations derived by Porod (1951, 1952) and by Debye, Anderson & Brumberger (1957) are generally used. According to one of these relations, frequently referred to as Porod's law, the intensity in the tail of the SAXS curve of structures with sharp phase boundaries decreases in proportion to \( s^{-4} \), where \( s \) is the radial coordinate in reciprocal space. This was confirmed to hold for catalysts and other porous substances, and of late was also found to apply to a number of semi-crystalline polymers in which the two phases are attributable to the simultaneous presence of crystallized and amorphous material.

However, recent investigations on ethylene-vinyl acetate copolymers in this laboratory yielded SAXS patterns showing distinct deviations from Porod's law, i.e. the intensity was found to decrease in proportion to \( s^{-6} \) rather than to \( s^{-4} \). The purpose of this paper is to indicate the methods by which the relevant information can be obtained from such patterns. This problem was studied by Blundell (1970), who derived relations for the intensities of the various orders of Bragg reflexions from layer structures in terms of deviations from the two-phase model; however, these relations appeared to be of little practical use for the analysis of these deviations. Recently, Ruland (1971) presented a method for analyzing deviations from Porod's law in terms of a model containing two phases connected by a transition layer in which the density varies regularly from the value in phase 1 to that in phase 2. Here some practical aspects of this method will be discussed; first however, a general relation will be derived which involves the mean square of the electron-density gradient and is applicable to general structures with continuous electron-density variations.

General relations

The following equation relates the amplitude \( F \) expressed in absolute units of the scattered X-rays at non-zero angles to the deviation \( \eta \) of the electron density from the mean value:

$$\eta(r) = \int F(s) \exp (2\pi i r \cdot s) d\nu = \mathcal{F} \{ F(s) \}.$$  

Here, \( r \) is a vector in real space with coordinates \( x, y \) and \( z \), \( s \) is a vector in reciprocal space with coordinates \( \xi, \eta, \zeta \); \( d\nu = d\xi \, d\eta \, d\zeta \) and \( \mathcal{F} \) is an operator indicating Fourier transformation. In this and the following equations the domain of integration in reciprocal space comprises the observed small-angle scattering, whereas in real space it comprises the irradiated volume of the sample. Differentiation of \( \eta(r) \) with respect to \( x \) leads to a vector whose magnitude is given by

$$\frac{\partial \eta}{\partial x} = \mathcal{F} \{ T(s) \}.$$  

where

$$T(s) = 2\pi i \xi F(s).$$

Application of Parseval's theorem* to (1) yields:

$$\int \left| \frac{\partial \eta}{\partial x} \right|^2 d\nu_x = \int |T|^2 d\nu_s.$$  

(2)

Similar expressions are found if \( \eta \) is differentiated with respect to \( y \) and \( z \); adding these to (2), replacing \( \xi^2 + \eta^2 + \zeta^2 \) by \( |s|^2 \) and \( (\partial \eta/\partial x)^2 + (\partial \eta/\partial y)^2 + (\partial \eta/\partial z)^2 \) by \( |\text{grad}\, \eta|^2 \) one gets:

$$4\pi^2 \int |s|^2 I(s) d\nu_s = \int |\text{grad}\, \eta|^2 d\nu_r.$$  

(3)

* The use of Parseval's theorem in this derivation was suggested by the referee.
which for isotropic structures equals

\[ 16\pi^3 \int s^4 J(s) ds = \int |\text{grad } \eta|^2 dv. \]  

(4)

This can be regarded as a parallel to the well known relation:

\[ 4\pi \int s^2 I(s) ds = \int \eta^2 dv. \]  

(5)

where \( \int s^2 I(s) ds \) is usually called the invariant. If absolute intensities are not available, the ratio \( R \) of (4) and (5) is useful:

\[ R = \frac{\langle |\text{grad } \eta|^2 \rangle}{\langle \eta^2 \rangle} = \frac{4\pi^2 \int s^4 J(s) ds}{6\pi^2 \int s^2 J(s) ds} \]  

(6)

Here \( J(s) \) is the intensity in arbitrary units and \( \bar{J}(s) \) the intensity as observed with slit collimation, using a primary beam of infinite height.

The ratio \( R \) is a useful parameter in the characterization of structures. In ideal two-phase structures, the gradient at the phase boundary is infinite and consequently \( R \) also goes to infinity. On the other hand, the minimum value of \( R = 4\pi^2/3 \) is reached if the intensity function \( J(s) \) consists of a single peak at \( s = s_0 \).

Such an intensity function would be obtained from a randomized layer structure in which the electron density perpendicular to the layers fluctuates according to a sine function. Apparently, this is the most gradual density variation attainable at a given value of \( \langle \eta^2 \rangle \).

To derive a general relation between \( R \) and the correlation function \( \gamma(r) \) the equation

\[ \gamma(r) = \frac{\int J(s) \exp(2\pi ir \cdot s) ds}{\int J(s) ds} \]

is differentiated twice with respect to \( x \). Passing to \( r = 0 \) then yields:

\[ \frac{\partial^2 \gamma}{\partial x^2} \bigg|_{r=0} = -4\pi^2 \frac{\int \xi^2 J(s) dv_s}{\int J(s) dv_s}. \]

If the sample is isotropic, this equation can be shown to be equivalent to

\[ \left( \frac{d^2 \gamma}{dr^2} \right) \bigg|_{r=0} = -\frac{4\pi^2}{3} \frac{\int s^4 J(s) ds}{\int s^2 J(s) ds} \]

which, by comparison with (6), leads to

\[ R = -3 \left( \frac{d^2 \gamma}{dr^2} \right) \bigg|_{r=0}. \]

If this is used to determine \( R \) from the correlation function, allowance must be made for the fact that the correlation function in the origin is very sensitive to experimental errors in the tail of the scattering curve, as has been pointed out by Caulfield & Ullman (1962).

### Pseudo two-phase structures

A pseudo two-phase structure is defined as consisting of two distinct phases, indicated by the subscripts 1 and 2, connected by a transition layer of width \( E \) in which the electron density varies gradually from \( \eta_1 \) to \( \eta_2 \). In the following it will be assumed that this variation is linear, as is schematically illustrated in Fig. 1(a).

In the definition of the respective volume fractions \( \phi_1 \) and \( \phi_2 \) the position of the phase boundary is chosen in the middle of the transition layer.

For such a pseudo two-phase structure the following relation holds:

\[ \langle |\text{grad } \eta|^2 \rangle = \Delta \eta^2 S/VE \]  

(7)

where \( \Delta \eta = \eta_1 - \eta_2 \) and \( S/V \) is the specific surface area of the phase boundary. According to Debye, Anderson & Brumberger (1957) \( S/V \) for a genuine two-phase structure can be found from the slope of the correlation function in the origin:

\[ (d\gamma/dr) \bigg|_{r=0} = -(S/4V) \langle \eta^2 \rangle \]  

(8)

As will be shown in the next section, this relation may also be applied to pseudo two-phase structures, provided the slope is taken at a distance of at least \( E \) away from the origin. Combination of (6), (7) and (8) then leads to

\[ E = -\frac{4}{R} (d\gamma/dr) \bigg|_{r=E}. \]  

(9)

Practical application of (9) involves calculation of the correlation function from the intensity function. Where absolute intensity measurements are available, this might be avoided by using Debye, Anderson & Brumberger's expression for \( d\gamma/dr \) given in equation (24) of their paper. However the computation of the correlation function generally does not present any difficulties and usually serves other purposes as well.

In a different approach to the study of pseudo two-phase structures, proposed by Ruland (1971), the electron-density fluctuations \( \eta(r) \) are looked upon as the convolution of the electron-density fluctuations \( g(r) \) in the corresponding ideal two-phase structure with a...
For the model given in Fig. 1(a), the function \( h(r) \) in the direction perpendicular to the phase boundary should be shaped as illustrated in Fig. 1(b). The corresponding intensity function is given by

\[
I(s) = I_\theta(s) I_h(s)
\]

where

\[
I_\theta(s) = \mathcal{F}\{\hat{g}\}
\]

and

\[
I_h(s) = \mathcal{F}\{\hat{h}\}.
\]

For the function presented in Fig. 1(b) one finds:

\[
I_h(s) = \frac{\sin 2\pi E s}{(2\pi E s)^2}.
\]

From (10) and (11) it follows that if \( E \) goes to zero, \( I(s) \) approaches \( I_\theta(s) \), which is the intensity that would have been obtained from the corresponding ideal two-phase structure. According to Porod’s law, in the tail region this is proportional to \( 1/s^4 \). Therefore, the intensity for the pseudo two-phase structure in this region is given by

\[
J(s) = c/s^4 \frac{\sin^2 \pi E s}{(\pi E s)^2}.
\]

where \( c \) is a constant. By expanding the sine function into a power series and ignoring all but the first and second terms, the slit-smeared intensity \( J \) can be approximated by

\[
\tilde{J}(s) = \frac{\pi c/2}{(1/s^3 - 2\pi^2 E^2/3s)}.
\]

This relation may be used to find \( E \) from a plot of \( s\tilde{J}(s) \) versus \( 1/s^2 \); an example of such a plot is given in Fig. 4, which is discussed further on.

A further quantity of interest for the study of pseudo two-phase structures is the value of \( \langle \eta^2 \rangle \). If \( E \) is smaller than the average radius of curvature of the phase boundary, this value may be calculated on the basis of a one-dimensional model like the one given in Fig. 1(a). For this model the following result is obtained:

\[
\langle \eta^2 \rangle = (\varphi_1 \varphi_2 - ES/6V)\Delta \eta^2.
\]

Lamellar pseudo two-phase structures

In the investigation of polymers containing layer structures, use can be made of the one-dimensional correlation function \( \gamma_1(x) \) (Kortleve & Vonk, 1968), which, for isotropic samples, can be obtained from the intensity function \( J(s) \) with the aid of the following equation:

\[
\gamma_1(x) = \frac{\int s^2 J(s) \cos (2\pi x s) ds}{\int s^2 J(s) ds}.
\]

This ‘observed’ correlation function may be compared with that calculated from a one-dimensional model, by means of the relation

\[
\gamma_1(x) = \frac{\int \eta(x) \eta(x - \xi) d\xi}{\int \eta^2(x) d\xi}.
\]

The calculation for a genuine two-phase layer structure was presented earlier (Vonk & Kortleve, 1967); in the following it will be shown how this calculation must be extended so as to make allowance for the presence of transition layers.

Let the electron-density variations perpendicular to the layers be represented by [Fig. 2(a)]:

\[
\eta(x) = \eta_1 + (\eta - \eta_1) P(x) D \varphi_1 D x.
\]

where \( P(x) \) is a function varying between 0 in phase 2 and 1 in phase 1. \( P(x) \) can be regarded as the convolution of the corresponding function \( f(x) \) for an ideal two-phase layer structure [Fig. 2(b)] with the function \( h(x) \) given in Fig. 1(b). Substitution of (15) in (14) yields:

\[
\gamma_1(x) = \frac{\int \tilde{f}(\xi) \tilde{f}(x - \xi - x_t) d\xi}{\int \tilde{f}^2(\xi) d\xi}.
\]

where \( D \) is the average distance of periodicity in the direction perpendicular to the layers. Since with \( E = 0 \), \( \tilde{f} \) equals \( \tilde{f} \) and \( \langle \eta^2 \rangle = \varphi_1 \varphi_2 \Delta \eta^2 \), this equation can be used to find \( \tilde{f} \) from the correlation function calculated for the ideal two-phase model. To determine the modified correlation function, \( \tilde{f} \) is convoluted with \( \tilde{h} \), which is then substituted back into (16). Here, for \( \langle \eta^2 \rangle \) expression (13) must be used, in which for layer structures the substitution

\[
S/V = 2/D
\]

must be made.

It can be shown that with \( E < x < x_1 \) the value of \( \tilde{f} \) is independent of \( E \) and equals \( \varphi_1 D - x \). Here \( x_1 \) is the distance at which interference between neighbouring layers of the same phase becomes important; this distance is of the order of the width of the thinnest layers present in the structure. Thus, from (16) one obtains

\[
\left( \frac{d\gamma_1}{dx} \right)_{E < x < x_1} = -(1/D) \left( \Delta \eta^2/\langle \eta^2 \rangle \right).
\]
On the condition that $x$ is small compared to the average radius of curvature of the phase boundary, this result should also be applicable to non-layer pseudo two-phase structures, provided that $1/D$ is replaced by $S/2V$ [equation (17)]. On the same condition the following relation holds:

\[
(dy_1/dx)_{x=0} = 2(dy_1/dr)_{r=0} \tag{19}
\]

which, combined with (18), leads to equation (8). Equations (8) and (18) may be used combined with equation (13) to determine the effect of $E$ on the slopes of the respective correlation functions near the origin. Particularly at small values of $\varphi_1$ or $\varphi_2$ this effect may be substantial.

**Practical aspect and applications**

Both methods for computing the width of the transition layer yield results that are sensitive to systematic errors in the tail of the SAXS curve. Therefore, special attention must be given to the separation of the SAXS intensity $J(s)$ or $\bar{J}(s)$ from the continuous background $J_b(s)$. Kortleve, Tuynman & Vonk (1972) found that under their circumstances of measurement, this background for polyethylene can be represented by

\[
J_b(s) = a + bs^n
\]

where $a$ and $b$ are constants and $n=4$. In order to achieve the separation from the background, a curve of this type was fitted to the experimental points at relatively large scattering angles, where the contribution of $\bar{J}(s)$ was felt to be negligible. In the present study this procedure was extended in such a way that other, even values of $n$ between 0 and 10 were allowed, of which the one ensuring the best fit of the curve to the experimental points was adopted. In Fig. 3 the $J_b$ curve thus obtained with $n=6$ is presented for a polypropylene sample.

A different assumption that can be made with regard to $J_b$ is, that it is constant in the region where $\bar{J}(s)$ contributes appreciably (e.g. Konrad & Zachmann, 1971). This corresponds to the horizontal line in Fig. 3. For both assumptions the value of $E$ was calculated by the method of Ruland; the two values, which are presented in Fig. 3, show but a relatively small difference. Apparently the sensitivity of the method to the way of correcting for the sample background is sufficiently moderate to allow meaningful results to be obtained.

In the application of the method involving computation of $\int s^nJ(s)ds$ it proved necessary to smooth the intensities in the tail of the SAXS curve obtained after subtraction of $J_b$ from the total intensities. In the case of pseudo two-phase structures the most effective way of achieving this is by making use of the curve in the $\bar{J}(s)$ versus $1/s^2$ plot, which for the polypropylene sample of Fig. 3 is shown in Fig. 4. As the smoothed values cannot be negative, the experimental points in the lower part of this figure scatter around the dashed line instead of around the drawn line. This is due to neglect of the third and higher terms in the series expansion of the sine functions which led to equation (12). Representing the straight line by the equation $\bar{J}(s) = p + q/s^2$, for values of $1/s^2$ between 0 and $-2p/q$ the broken line may be described by $\bar{J}(s) = q/2/(4ps^2)$.

The one-dimensional correlation function $\gamma_1(0)$ for the same sample is presented in Fig. 5. The effect of the transition layers manifests itself in the displacement of the straight portion of the correlation function from the origin to the region between 10 and 20Å; the slope in this part, which according to equation (9) is needed for calculating $E$, is indicated by a dashed line. The same figure also shows the calculated one-dimensional correlation function $\gamma_1$ giving the best fit with the experimental one. In this calculation (Vonk & Kortleve, 1967), the crystallinity $\Phi$ was taken equal to 0.36, whereas the distribution functions $P_c$ and $P_s$ were Gauss functions of integral breadths equal to $B_c = 1.0 \cdot \Phi$ and $B_s = 1.0 \cdot (1 - \Phi)$ respectively. The preliminary result for the ideal two-phase structure was

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* Apart from (19), the following relations between $\gamma_1$ and $\gamma$ may be directly obtained from the definitions:

\[
\gamma_1(x)_{x=0} = d\langle \gamma(r) \rangle/dr,
\]

\[
(d\gamma_1/dx)_{x=0} = 3(d\gamma/dr)_{r=0}.
\]

It should be emphasized that $\gamma_1$ is of physical significance only for those distances which are small compared to the average radius of curvature of the phase boundary.

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**Fig. 3.** Intensity from a polypropylene sample at intermediate scattering angles. Two alternative ways of drawing the background are indicated.
modified according to equation (16), using \( E = 9.7 \, \text{Å} \) and \( D = 125 \, \text{Å} \).

The persistent deviations between \( \gamma_{\text{obs}} \) and \( \gamma_{\text{calc}} \) observed in this and other cases, are of two types: at first the slope near the origin in \( \gamma_{\text{obs}} \) is nearly always found to exceed that in \( \gamma_{\text{calc}} \) and, secondly, \( \gamma_{\text{obs}} \) damps out much more rapidly than \( \gamma_{\text{calc}} \). The first type of discrepancy can be explained by assuming the phase boundary to be corrugated; this would result in a larger specific surface area and, as a consequence of equation (8), in a larger slope of \( \gamma_{\text{calc}} \) near the origin. In the present case, the specific surface area would be about 1.3 times that of the corresponding ideal layer structure. The increased rate of damping out may be bound up with non-parallelism between neighbouring layers of the same type; however more theoretical work is needed in order to obtain quantitative information on this point.

Table 1 presents the results found by applying both methods for calculating \( E \) to a number of polymers. The SAXS curves of these polymers were registered by means of a Kratky camera with counting equipment; monochromation was simulated with the aid of a \( \beta \) filter and pulse-height discrimination. The intensity profile of the primary beam was such that, at scattering angles up to \( 4^\circ \), it could be considered to be of infinite height.

Table 1 shows the \( D \) values derived from the position of the first subsidiary maximum in the correlation functions.

\( E_i \) is the value of \( E \) obtained from equation (9) and \( E_{II} \) the one obtained according to the method of Ruland. The relatively good agreement between \( E_i \) and \( E_{II} \) probably must be attributed partly to the fact that for the calculation of \( E_i \) the intensities in the tail of the diffraction curve were smoothed with the aid of the \( s\tilde{J}(s) \) versus \( 1/s^2 \) plot (Fig. 4), which was also used for the determination of \( E_{II} \).

If, for the time being, the possible corrugation of the layers is disregarded, the value of \( 2E/D \) in the last column represents the volume fraction occupied by the transition layers and hence can be looked upon as a preliminary measure of the deviation from the ideal two-phase structure. From duplo determinations, as well as from considerations like those given in connexion with Fig. 3, the accuracy of \( 2E/D \) is estimated to amount to 2–3\% (standard deviation).

The \( 2E/D \) values for the samples 1–8 of polyethylene and its copolymers appear to increase with increasing chain branching. In none of the other homopolymers (samples 9–14) the phase boundaries are as sharp as in linear polyethylene; however the two-phase character invariably predominates, and a description of the structure in terms of a single phase ‘crystal defect’ model seems out of place. The solvent cast elastomers 15 and 16 show a remarkably sharp phase boundary; this is in accord with electron-microscopic photographs of these samples, which also show well separated phases.

**Conclusion**

This work shows that SAXS studies permit the detection of deviations from the ideal two-phase structure and enable these to be expressed in a quantitative way, either by calculation of \( \langle |\text{grad} \eta| \rangle \) or by the method put forward by Ruland (1971). It is felt that if these deviations are relatively large, or if continuous density variations occur in the sample, the former method is to be preferred. In the study of polymers however, Ruland’s method will generally be applicable.

For the evaluation of polymer structures, a Fortran V computer program has been written, covering separation of the background, fitting of the intensity data in the tail in a \( s\tilde{J}(s) \) versus \( 1/s^2 \) plot, calculation of \( \langle |\text{grad} \eta| \rangle \) and \( \langle |\text{grad} \eta| \rangle \), desmearing according to the procedure described by Vonk (1971) and calculation of the ob-
Table 1. Determination of the thickness \( E \) of the transition layer in various polymers

<table>
<thead>
<tr>
<th>Number</th>
<th>Description of the sample</th>
<th>Density ((\text{g cm}^{-3}))</th>
<th>( D ) (Å)</th>
<th>( E_1 ) (Å)</th>
<th>( E_2 ) (Å)</th>
<th>( 2E/D ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Linear polyethylene, Marlex 6009 (Philips) Quenched from the melt</td>
<td>0.966</td>
<td>275</td>
<td>10</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Linear polyethylene, very high M.W. (experimental) Slowly crystallized from the melt</td>
<td>0.979</td>
<td>410</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Short-chain branched polyethylene, Stamylan 1500 (DSM) Quenched from the melt</td>
<td>0.918</td>
<td>110</td>
<td>9</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>Slowly crystallized from the melt</td>
<td>0.923</td>
<td>125</td>
<td>13</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Copolymer (ethylene-vinyl acetate) (experimental) 2-2 mol. % vinyl acetate</td>
<td>0.949</td>
<td>100</td>
<td>21</td>
<td>25</td>
<td>46</td>
</tr>
<tr>
<td>6</td>
<td>10 mol. % vinyl acetate</td>
<td>0.934</td>
<td>120</td>
<td>11</td>
<td>11</td>
<td>19</td>
</tr>
<tr>
<td>7</td>
<td>Polypropylene–Carlona (Shell)</td>
<td>0.904</td>
<td>125</td>
<td>10</td>
<td>10</td>
<td>16</td>
</tr>
<tr>
<td>8</td>
<td>Poly(ethylene-terephthalate)</td>
<td>0.898</td>
<td>130</td>
<td>13</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>9</td>
<td>Hostadur AVP 400 (Hoechst)</td>
<td>1.359</td>
<td>85</td>
<td>10</td>
<td>11</td>
<td>25</td>
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<tr>
<td>10</td>
<td>Experimental polymer</td>
<td>1.391</td>
<td>100</td>
<td>12</td>
<td>13</td>
<td>25</td>
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<tr>
<td>11</td>
<td>Nylon 6, cast.</td>
<td>1.164</td>
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<td>13</td>
<td>33</td>
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<tr>
<td>12</td>
<td>Experimental polymer</td>
<td>1.141</td>
<td>80</td>
<td>8</td>
<td>7</td>
<td>20</td>
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<tr>
<td>13</td>
<td>Block copolymer MMA—I–MMA*), solvent cast</td>
<td>0.908</td>
<td>705</td>
<td>15</td>
<td>15</td>
<td>4</td>
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<tr>
<td>14</td>
<td></td>
<td>0.974</td>
<td>460</td>
<td>11</td>
<td>16</td>
<td>6</td>
</tr>
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</table>

* MMA = methyl metacrylate, I = isoprene


References: