

## ORIGINAL ARTICLE

# Static partial scattering functions for linear and ring random copolymers

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The static partial scattering functions for linear and ring random copolymers of type A–B are investigated. In the case of random distribution of the different kinds of monomers, analytic forms can be derived. Monte Carlo simulations are used to make evaluations on biased distributions of the different kinds of monomers. Results clearly show that the number, fraction and distribution of monomers have significant effect on the scattering intensities at  $Q \times R_g > 1$ , where  $Q$  is the magnitude of the scattering vector and  $R_g$  is the radius of gyration of the polymer. The scattering function in molten state is also calculated on the basis of random phase approximation.

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**Keywords:** monte carlo simulation; partial scattering function; random copolymer; random phase approximation; ring polymer; small-angle scattering

## INTRODUCTION

Development of a variety of polymers with specific molecular architecture, for example block and graft copolymers (for recent reviews on block and graft copolymer, see Hamley<sup>1</sup> and Lodge<sup>2</sup>), star polymer (for recent reviews on star polymer, see Mishra<sup>3</sup> and Grest<sup>4</sup>), dendrimer,<sup>5</sup> polyrotaxane<sup>6</sup> and so on, has been the mainstream in polymer science for advanced applications (for recent reviews on designed polymerization, see Hatada<sup>7</sup> and Odian<sup>8</sup>). Therefore, an investigation of the static configuration of these polymers is fundamental to the field and has been of intensive interest.

Historically, Flory<sup>9</sup> first predicted that the static configuration of linear polymers on the melt obeys the Gaussian statistic, which was proved by small-angle neutron scattering with protonated polymers in a deuterated polymer matrix.<sup>10</sup> Since then, many types of polymers have been identified by their static structures with the small-angle neutron scattering technique, and the contemporary theoretical progress in small-angle scattering has been of importance.<sup>11</sup>

In this study, the static scattering contributions from different kinds of monomer units in linear and ring random copolymers, which have hardly been given attention, are discussed. We assume random copolymers consisting of two different kinds of monomer units, namely monomer-A and monomer-B. The static partial scattering functions of the monomer-A component, that is, the scattering contribution from monomer-A units, in linear and ring copolymers are derived on the basis of Gaussian statistics. Monte Carlo simulation is applied to evaluate the array of monomers. The scattering function of the molten random copolymers of type A–B is also discussed.

## SCATTERING THEORY

### Linear random copolymer

Let us begin with the Debye function for the linear Gaussian polymer consisting of  $N$  segments with the segment length  $b$ ,<sup>12</sup> that is,

$$S_{\text{Debye}}(Q) = \frac{1}{N^2} \int_0^N dm \int_0^N dn \exp\left\{-\frac{Q^2 b^2}{6} |m - n|\right\} \quad (1)$$
$$= \frac{2}{Q^4 R_g^4} \{\exp(-Q^2 R_g^2) - 1 + Q^2 R_g^2\}$$

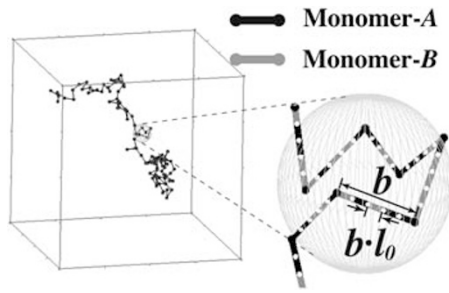
with the magnitude of scattering vector  $Q (= 4\pi \sin(\theta/2)/\lambda)$ , scattering angle  $\theta$ , wavelength of incident beam  $\lambda$ ) and the radius of gyration of the linear polymer  $R_g$  given by

$$R_g = \sqrt{\frac{Nb^2}{6}} \quad (2)$$

In the above description, the total length  $L$  of the linear polymer can be defined as  $L = Nb$ .

As the first step, Equation (1) is discretized with the interval  $l_0$ , namely,

$$S_{\text{Debye}}^{\text{Linear}}(Q) = \frac{1}{N^2} \sum_{i=0}^{n_0-1} \sum_{j=0}^{n_0-1} \int_{i_0 \cdot l_0}^{(i_0+1) \cdot l_0} dm \int_{j_0 \cdot l_0}^{(j_0+1) \cdot l_0} dn \exp\left\{-\frac{Q^2 b^2}{6} |m - n|\right\} \quad (3)$$



**Figure 1** Schematic picture of a random copolymer consisting of a random sequence of 50% monomer-A and 50% monomer-B, where the segment length is  $b$  and the monomer length is  $b \times l_0$ . The polymer is generated by 3D-random walks with 100 steps.

where  $i$  and  $j$  are natural numbers and  $n_0$  is related to the interval  $l_0$  as  $l_0 = N/n_0$ .  $n_0$  roughly corresponds to the polymerization degree (the number of monomer units within the single polymer chain) by assuming that the lengths of monomer-A and monomer-B are the same. In this case,  $b \times l_0$  is equivalent to the length of the single monomer unit. In our model, one segment of a Gaussian chain may hypothetically contain a number of monomers. In the case of flexible polymers,  $l_0$  is very close to unity, and  $l_0 < 1$  corresponds to semi-flexible or rigid polymers. Figure 1 schematically depicts the model of a linear random copolymer.

To reflect the distribution of monomer-A units, Equation (3) is modified as follows

$$S_{\text{Debye}}^{\text{Linear}}(Q) = \frac{1}{N^2} \sum_{i=0}^{n_0-1} \sum_{j=0}^{n_0-1} \langle A_m(i) A_n(j) \rangle \int_{i_0 \cdot l_0}^{(i_0+1) \cdot l_0} dm \int_{j_0 \cdot l_0}^{(j_0+1) \cdot l_0} dn \exp \left\{ -\frac{Q^2 b^2}{6} |m-n| \right\} \quad (4)$$

where  $A_{m,n}(k)$  is a  $n_0$ -dimensional vector defined by

$$A_{m,n}(k) = \begin{cases} 1 & (\text{monomer-A exist}) \\ 0 & (\text{monomer-B exist}) \end{cases} \quad (5)$$

for the  $k$ -th interval. The ensemble average  $\langle A_m(i) \cdot A_n(j) \rangle$  is given by

$$\langle A_m(i) \cdot A_n(j) \rangle = \begin{cases} \Phi_A & (\text{for } i=j) \\ \Phi_A^2 & (\text{for } i \neq j) \end{cases} \quad (6)$$

with the length fraction of the monomer-A component,  $\Phi_A$ .

In the case of a purely random process for the distribution of monomers, we can substitute  $\langle A_m(i) \cdot A_n(j) \rangle$  for  $A_m(i) \cdot A_n(j)$  in Equation (4), and in this condition, an analytic form of Equation (4) can be obtained as follows

$$S_{\text{Discr}}^{\text{Linear}}(Q) = \frac{2}{x^2} \left[ \exp(-x) - 1 - n_0 \exp\left(-\frac{x}{n_0}\right) + n_0 + \left\{ n_0 \exp\left(-\frac{x}{n_0}\right) - n_0 + x \right\} / \Phi_A \right] / N_l \quad (7)$$

with  $x = Q^2 R_{gr}^2$  and  $N_l = 1 + (1 - \Phi_A) / (\Phi_A n_0)$ .

### Ring random copolymer

The above treatment can be applied to the ring polymer. On the basis of Gaussian statistics, the form factor of the ring polymer

is given by<sup>13</sup>

$$S_{\text{Ring}}(Q) = \frac{1}{N^2} \int_0^N dm \int_0^N dn \exp \left[ -\frac{Q^2 b^2}{6} \left\{ |m-n| - \frac{(m-n)^2}{N} \right\} \right] = \frac{\sqrt{2}}{QR_{gr}} \cdot D\left(\frac{QR_{gr}}{\sqrt{2}}\right) \quad (8)$$

where  $D(u)$  is the Dawson function, that is,  $D(u) = \exp(-u^2) \int_0^u \exp(t^2) dt$ , and  $R_{gr}$  is the radius of gyration for the ring polymer defined by

$$R_{gr} = \sqrt{\frac{Nb^2}{12}} \quad (9)$$

Thereafter, the discretization and summation for the purely random process of the distribution of monomers are executed for the length fraction of the monomers,  $\Phi_A$ , in the same way as in Equations (3)–(7), and after some derivations, we obtain

$$S_{\text{Discr}}^{\text{Ring}}(Q) = \frac{1}{N^2} \sum_{i=0}^{n_0-1} \sum_{j=0}^{n_0-1} \langle A_m(i) A_n(j) \rangle \int_{i_0 \cdot l_0}^{(i_0+1) \cdot l_0} dm \int_{j_0 \cdot l_0}^{(j_0+1) \cdot l_0} dn \times \exp \left[ -\frac{Q^2 b^2}{6} \left\{ |m-n| - \frac{(m-n)^2}{N} \right\} \right] = \frac{1}{2x} \left[ \left\{ n_0 - \sqrt{2x}(n_0 - 2) \cdot D\left(\sqrt{\frac{x}{2}}\right) - F \right\} / \Phi_A - \left\{ n_0 - \sqrt{2x} \cdot n_0 \cdot D\left(\sqrt{\frac{x}{2}}\right) - F \right\} / N_r \right] \quad (10)$$

where

$$F = \exp \left\{ \frac{2x}{n_0} \left( \frac{1}{n_0} - 1 \right) \right\} \times \left\{ n_0 - \sqrt{2x}(n_0 - 2) \cdot D\left(\sqrt{\frac{x}{2}} \left( 1 - \frac{2}{n_0} \right)\right) \right\} \quad (11)$$

with  $x = Q^2 R_{gr}^2$  and  $N_r = 1 + (1 - \Phi_A) / (\Phi_A n_0)$ .

## RESULTS AND DISCUSSION

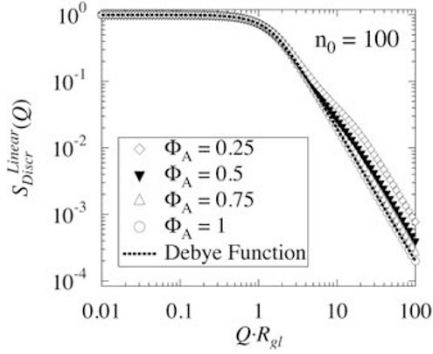
### Behavior of $S_{\text{Discr}}^{\text{Linear}}(Q)$ and $S_{\text{Discr}}^{\text{Ring}}(Q)$

The effects of the parameters  $\Phi_A$  and  $n_0$  ( $=N/l_0$ ) on  $S_{\text{Discr}}^{\text{Linear}}(Q)$  in Equation (7) are examined in Figure 2 and Figure 3. It is clearly seen that the normalized scattering function is hardly affected by  $\Phi_A$  and  $n_0$  for  $QR_{gr} < 1$ , whereas excess scattering intensity arises with decreasing  $\Phi_A$  and/or  $n_0$  for  $QR_{gr} > 1$ .

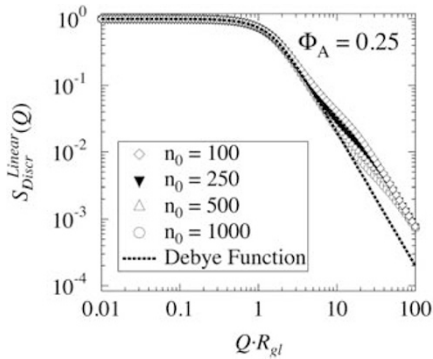
In Figure 4,  $S_{\text{Ring}}(Q)$  values given by Equation (8) are clarified with  $S_{\text{Debye}}(Q)$  values given by Equation (1), where  $Q \times R_{gr}$  for  $S_{\text{Debye}}(Q)$  is multiplied by  $\sqrt{2}$  to compare the shape of the curves. The essential difference between  $S_{\text{Debye}}(Q)$  and  $S_{\text{Ring}}(Q)$  is the curvature at  $Q \approx 1/R_{gr}$ , that is, the curvature of  $S_{\text{Ring}}(Q)$  is greater than that of  $S_{\text{Debye}}(Q)$ . The dependence of  $\Phi_A$  and  $n_0$  on  $S_{\text{Discr}}^{\text{Ring}}(Q)$  in Equation (10) is similar to  $S_{\text{Discr}}^{\text{Linear}}(Q)$ , that is, excess scattering is observed for  $QR_{gr} > 1$  with decreasing  $\Phi_A$  and/or  $n_0$  as exhibited in Figure 4.

### Effect of biased monomer distribution

The effect of the distribution of monomers can be investigated by Monte Carlo simulation. We define the conditional probability that two monomer-A units are successively placed as  $\phi_{AA}$ , as well as the conditional probability that a monomer-A unit and a monomer-B unit are successively placed as  $\phi_{AB}$ . Thereafter,  $\Phi_A$ ,  $\phi_{AA}$  and  $\phi_{AB}$  are



**Figure 2** Normalized partial scattering functions for linear random copolymers given by Equation (7) with different  $\Phi_A$  as a function of  $QR_g$ :  $\Phi_A=0.25$  ( $\diamond$ );  $\Phi_A=0.5$  ( $\blacktriangledown$ );  $\Phi_A=0.75$  ( $\triangle$ );  $\Phi_A=1$  ( $\circ$ ); the normalized Debye function given by Equation (1) (---). The fixed parameter is  $n_0$  (=100).



**Figure 3** Normalized partial scattering functions for linear random copolymers given by Equation (7) with different  $n_0$  as a function of  $QR_g$ :  $n_0=100$  ( $\diamond$ );  $n_0=250$  ( $\blacktriangledown$ );  $n_0=500$  ( $\triangle$ );  $n_0=1000$  ( $\circ$ ); the normalized Debye function given by Equation (1) (---). The fixed parameter is  $\Phi_A$  (=0.25).

related as follows

$$\phi_{AB} = \frac{\Phi_A}{1 - \Phi_A} (1 - \phi_{AA}) \quad (12)$$

In this simple model,  $\Phi_A < \phi_{AA}$  indicates that monomer-A units tend to neighbor; similarly,  $\Phi_A > \phi_{AA}$  indicates that monomer-A units are distributed separately.  $A_{m,n}(k)$  in Equation (4) is determined by generating random numbers  $\phi_k$  between 0 and 1 as follows,

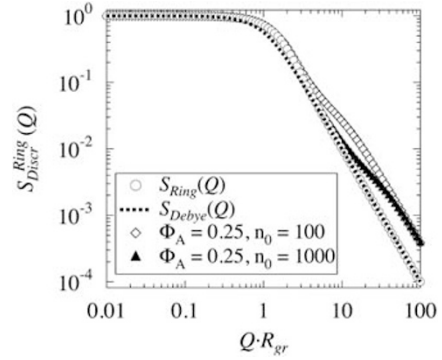
$$A_{m,n}(k) = \begin{cases} 1 & (\text{for } \phi_k \leq \phi_{AA}) \\ 0 & (\text{for } \phi_k > \phi_{AA}) \end{cases} \quad (13)$$

in the case of  $A_{m,n}(k-1)=1$ , and

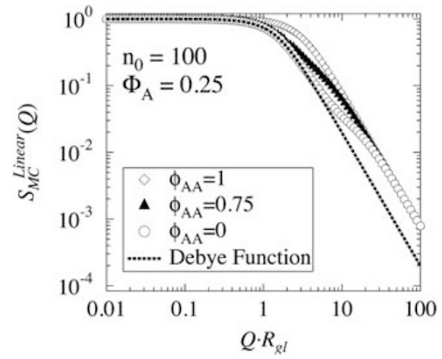
$$A_{m,n}(k) = \begin{cases} 1 & (\text{for } \phi_k \leq \phi_{AB}) \\ 0 & (\text{for } \phi_k > \phi_{AB}) \end{cases} \quad (14)$$

in the case of  $A_{m,n}(k-1)=0$ .

In Figure 5, the results of Monte Carlo simulations by changing  $\phi_{AA}$  with  $n_0=100$  and  $\Phi_A=0.25$  are exhibited. Sampling was repeated until the relative variation between  $n$ -th and  $(n+1)$ -th step became less than  $10^{-5}$ . Otherwise,  $S_{MC}^{\text{Linear}}(Q)$  was the average of  $10^4$  samplings. The partial scattering function,  $S_{MC}^{\text{Linear}}(Q)$ , is affected only at  $QR_g > 1$ , and the additional scattering intensity arises with increasing  $\phi_{AA}$ .  $S_{MC}^{\text{Linear}}(Q)$  with  $\phi_{AA}=1$  coincides with the Debye function



**Figure 4** Normalized partial scattering functions for ring random copolymers given by Equation (10) with different  $n_0$  and  $\Phi_A$  as a function of  $QR_g$ :  $\Phi_A=1$  ( $\circ$ ); the normalized Debye function given by Equation (1) (---);  $\Phi_A=0.25$  and  $n_0=100$  ( $\diamond$ );  $\Phi_A=0.25$  and  $n_0=1000$  ( $\blacktriangle$ ).



**Figure 5** Normalized partial scattering functions for linear random copolymers obtained by Monte Carlo simulation with different  $\phi_{AA}$  as a function of  $QR_g$ :  $\phi_{AA}=1$  ( $\diamond$ );  $\phi_{AA}=0.75$  ( $\blacktriangle$ );  $\phi_{AA}=0$  ( $\circ$ ); the normalized Debye function given by Equation (1) (---). The fixed parameters are  $n_0$  (=100) and  $\Phi_A$  (=0.25).

$S_{\text{Debye}}(Q) = 2\{\exp(-x) - 1 + x\}/x^2$  with  $x = Q^2 R_g^2 \Phi_A$ . The results obviously confirm that the alignment of different kinds of monomers is also an important condition for the partial scattering function.

### Molten state

The scattering function for molten copolymers can be calculated on the basis of random phase approximation (RPA).<sup>14</sup> For instance, static scattering functions for multiblock copolymers with various architectures in the molten state were obtained by RPA.<sup>15</sup> In the case of the linear random copolymer of monomer-A and monomer-B with random monomer distribution, RPA leads to the scattering function as

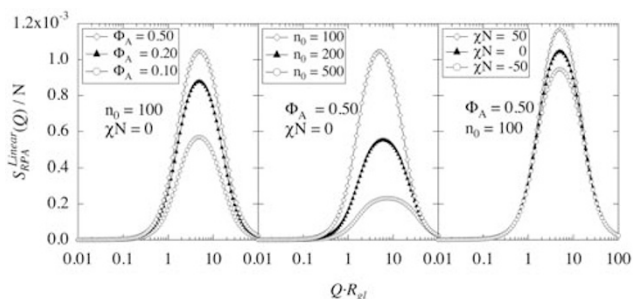
$$S_{\text{RPA}}^{\text{Linear}} = \frac{N}{S - 2\chi N} \quad (15)$$

with

$$S = \frac{S_{11} + 2S_{12} + S_{22}}{S_{11} \cdot S_{22} - S_{12}^2} \quad (16)$$

where  $N$  is the segment number and

$$\begin{aligned} S_{11} &= \Phi_A^2 \cdot S_{\text{Discr}}^{\text{Linear}}(x, \Phi_A, n_0) \\ S_{22} &= (1 - \Phi_A)^2 \cdot S_{\text{Discr}}^{\text{Linear}}(x, 1 - \Phi_A, n_0) \\ S_{12} &= \Phi_A(1 - \Phi_A) \cdot S_{\text{Debye}}(x) \end{aligned} \quad (17)$$



**Figure 6** Scattering intensities for molten random linear copolymers of type  $A-B$  given by Equations (15)–(17) with the monomer- $A$  fraction,  $\Phi_A$ , the monomer number,  $n_0$ , and the Flory–Huggins segment–segment interaction parameter,  $\chi$ , as a function of  $QR_g$ : (left)  $\Phi_A$  dependence by fixing  $n_0=100$  and  $\chi=0$ :  $\Phi_A=0.50$  ( $\diamond$ );  $\Phi_A=0.20$  ( $\blacktriangle$ );  $\Phi_A=0.10$  ( $\circ$ ); (center)  $n_0$  dependence by fixing  $\Phi_A=0.50$  and  $\chi=0$ :  $n_0=100$  ( $\diamond$ );  $n_0=200$  ( $\blacktriangle$ );  $n_0=500$  ( $\circ$ ); (right)  $\chi$  dependence by fixing  $\Phi_A=0.50$  and  $n_0=100$ :  $\chi N=50$  ( $\diamond$ );  $\chi N=0$  ( $\blacktriangle$ );  $\chi N=-50$  ( $\circ$ ); with the segment number  $N$ .

with  $x=Q^2R_g^2$ , and  $S_{\text{Debye}}(x)$  and  $S_{\text{Discr}}^{\text{Linear}}(x, \Phi_A, n_0)$  are defined by Equations (1) and (7), respectively. The other parameters are the Flory–Huggins segment–segment interaction parameter,  $\chi$ , the length fraction of monomer- $A$ ,  $\Phi_A$  and the number of monomer units,  $n_0$ . In Figure 6, the parametric calculations with Equations (15)–(17) are shown, where the tested parameters are  $\Phi_A$ ,  $n_0$  and  $\chi$ . In the case of  $\Phi_A$  dependence, see Figure 6 left, peak heights were only affected, that is, the highest peak is given by  $\Phi_A=0.50$  and the heights decreased with  $\Phi_A \rightarrow 0$  and  $\Phi_A \rightarrow 1$ , whereas the peak widths and peak positions were the same for each  $\Phi_A$ . On the other hand, both the peak heights, peak widths and peak positions were evidently affected by different  $n_0$  values as shown in Figure 6 center, where the peak heights were decreased with increasing  $n_0$ , and at the same time, the peak widths broadened and the peak positions shifted to a higher  $Q$ . The  $\chi$  dependence was similar to the linear polymer blends, that is, the peak height with larger  $\chi$  was higher than that of smaller  $\chi$ , and the peak width with larger  $\chi$  was narrower than that of smaller  $\chi$ , as exhibited in Figure 6 right.

### Experimental feasibility

The experimental observation of such behaviors is feasible, for example, by contrast matched or contrast variation neutron scattering experiments with partially deuterated random copolymers.<sup>11</sup> In the case of small-angle neutron scattering (SANS), the observable highest- $Q$  of the usual diffractometers with pinhole collimators and a constant neutron wavelength is limited, for example, the limitation of SANS-U diffractometer at JRR-3 in Japan is  $Q_{\text{MAX}} \approx 0.2 \text{ \AA}^{-1}$  with  $\lambda=7 \text{ \AA}$ .<sup>16</sup> To examine the difference between a random copolymer and the corresponding homopolymer by SANS, the radius of gyration,  $R_g$ , (that is, the molecular weight) of the measured polymer should be absolutely large. For example,  $R_g$  of polystyrene with molecular weight  $40 \text{ kg mol}^{-1}$  in the  $\theta$ -condition is  $57 \text{ \AA}$ ,<sup>17</sup> which gives  $Q=0.175 \text{ \AA}^{-1}$  for  $Q \times R_g=10$ . Therefore, we believe that experimental verification with a usual SANS diffractometer is possible. Future time of flight SANS diffractometers at the second generation spallation neutron sources will be certainly useful for the purpose, as diffractometers can cover a higher  $Q$ -range ( $Q_{\text{MAX}} \sim 50 \text{ \AA}^{-1}$ ).<sup>18</sup>

### CONCLUSIONS

The static partial scattering functions for linear and ring random copolymers were evaluated. In the case of random distribution of monomers, analytic forms were obtained. Monte Carlo simulation was

used to verify the effects on biased distribution of the monomers. Results clearly showed that the number, fraction and distribution of monomers have a significant effect on the scattering intensities at  $QR_g > 1$ , which could be examined by scattering experiments.

In the case of molten state, scattering intensity was obtained by random phase approximation. The appearance of a single peak was numerically predicted, which has an analogy to block copolymers of type  $A-B$ . It was shown that the shape, height and position of the peak were affected by the three parameters, namely, fraction, number of monomers and the Flory–Huggins segment–segment interaction parameter.

Furthermore, the mathematical treatments and methodology achieved in the article can be applied for the detailed analyses of random copolymers of semiflexible non-Gaussian chains with the helical wormlike chain model,<sup>19</sup> distribution of beaded molecules in polyrotaxane<sup>20,21</sup> and so on by means of small-angle scattering.

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