

Small-angle light scattering studies of poly(*N*-vinylcarbazole)

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Morphology of PVK samples cast from various solvents (cyclohexanone, tetrahydrofuran, benzene) and crystallized on a glass surface, was studied by means of SALS. Results show existence of rod-like elements forming a morphology with nonrandom correlations of orientations. This morphology is practically independent of crystallization conditions.

Keywords Poly(*N*-vinylcarbazole); light scattering; crystalline morphology; rod-like structure

INTRODUCTION

The interest of many laboratories being focused on poly(*N*-vinylcarbazole) is due mainly to its photoconductivity properties. Fields of research cover the methods of synthesis of PVK as well as properties of the polymer. Both aspects have recently been reviewed by Penwell *et al.*¹ In recent years some papers dealing with mechanisms of conductivity, photoconductivity and fluorescence of PVK have been published¹⁻⁴. It can be presumed that the electrical properties of the polymer might be affected by its physical structure.

A number of papers have already been published concerning the investigation of the crystallographic structure by means of X-ray, or electron diffraction and studies on the morphology of the polymer by means of optical microscopy^{5-7,9-11}. A quantitative description of the morphology can be achieved by means of small-angle-light scattering (SALS)⁸. This method was recently applied to studies of PVK⁹⁻¹¹. In all cases, however, oriented samples of the polymer were investigated, and no reference was made to the isotropic state.

This report is a preliminary study of correlations between some aspects of sample history or structure and its electrical properties. The scope of this work was to investigate the effect of conditions of sample formation on its morphology by means of SALS. A semi-quantitative description of the morphology is also attempted.

EXPERIMENTAL

Synthesis

PVK samples were obtained by radiation induced polymerization. This process was performed in the molten state by γ -irradiation, at 96°C, from a Co⁶⁰ source 'Gamma-cell 220'. Polymerization was carried out under a nitrogen atmosphere. The polymer was purified by means of multiple precipitation with methanol from a benzene solution and in addition the polymer was fractionated in an extraction column, and one fraction

was used for further studies.

The molecular weight was determined from the intrinsic viscosity, η , measured from the viscometry of benzene solutions at 25°C applying the formula^{1,2}:

$$[\eta] = 3.05 \cdot 10^{-2} \cdot M^{0.58} \quad ([\eta] \text{ is given in ml/g})$$

$M_n = 9.6 \cdot 10^5$ for the investigated fraction. The glass transition temperature, as determined by d.t.a., was 227°C, which is consistent with values given in refs. 18 and 19.

Sample preparation

Foils, 2-4 microns thick, were cast on glass from solutions in cyclohexanone, tetrahydrofuran or benzene. After preliminary evaporation of the solvent (24 hours at room temperature) samples were dried in a vacuum at 120°C. The foils were transparent and showed no SALS pattern. Samples were crystallized for 2-4 h in a high vacuum (10^{-5} Th) or in silicone oil at temperatures: 240°, 300°, 320°, 350°C.

In all cases crystallinity was detected by means of WAXD. Usually the diffraction patterns exhibited a strong sharp line at $2\theta = 8.4^\circ$ (see *Figure 1*) corresponding to spacing $d = 10.4 \text{ \AA}$, which could be identified as reflexion from (1010) crystallographic plane⁵⁻⁷. This line is superimposed on the wide amorphous halo of relatively low intensity (A_1). The second amorphous halo, A_2 , of much lower intensity, is visible at $2\theta = 20^\circ$. This is consistent with ref. 6, and indicates a relatively high crystallinity of the samples studied.

Studies on morphology

SALS patterns were obtained using standard apparatus equipped with an He-Ne laser. Patterns were recorded on photographic films, using both H_v and V_v polarization modes. The angular distribution of intensity was analysed using a recording microphotometer.

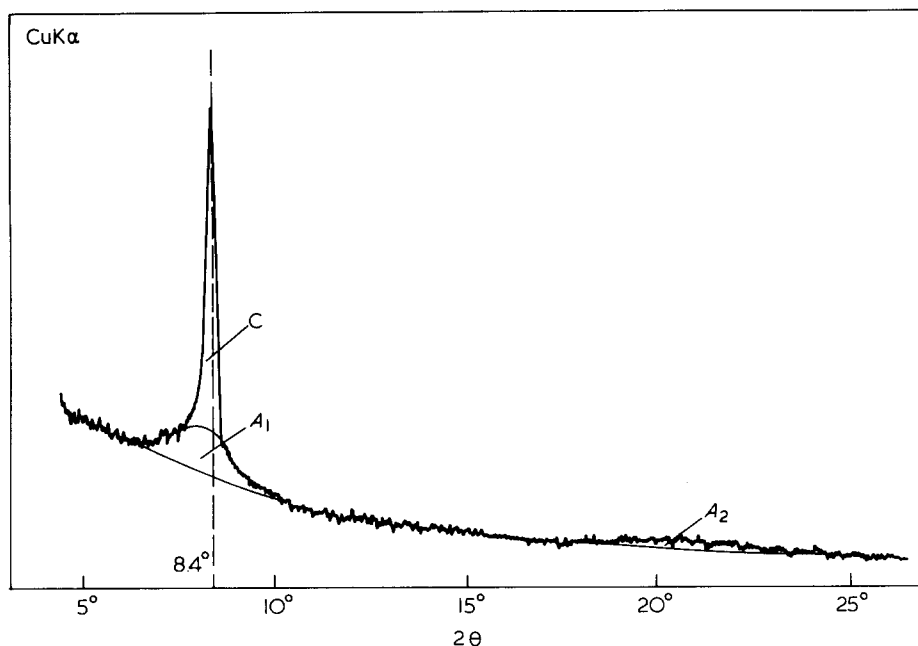


Figure 1 X-Ray diffraction pattern from PVK sample crystallized on glass surface. C denotes the narrow crystalline line, A_1 and A_2 are two bands of amorphous scattering

RESULTS AND DISCUSSION

Typical SALS patterns are presented in Figure 2. It is quite surprising that in all cases the light scattering patterns obtained from the variously treated samples appear to be identical concerning both the shape of the pattern and the character of the angular distribution of intensity. This means that neither the crystallization temperature nor the chemical character of the solvent affect the scattering pattern. Therefore, it can be concluded that, in the present case, the level of morphology evaluated by means of light scattering, is independent of crystallization conditions.

This behaviour of PVK samples is quite different from the behaviour of many other polymers, which usually show morphology dependence upon the factors mentioned. We cannot offer any reasonable explanation for this observed phenomena.

Taking into account, however, that the range of crystallization temperatures studied covered a large part of the distance between the glass transition and the melting temperatures, it may be suggested that chemical structure of the molecular repeating unit or structure of the crystallographic unit cell, rather than crystallization conditions, determine the morphology of the studied PVK fraction.

As one also can see, in Figure 2 the patterns are unusual: at first both H_V and V_V patterns are rotated through 45° with respect to the polarization planes. However, the H_V pattern appears to have a two-fold symmetry instead of four-fold symmetry, whereas the V_V pattern exhibits unusual four-fold symmetry. The first feature is well known^{13,14}, and usually explained as a result of optic axes tilting with respect to the geometric axis of the structural element; the second feature requires some explanation. Figure 3b shows photometric traces from a H_V light scattering pattern along the 0° and 90° azimuthal

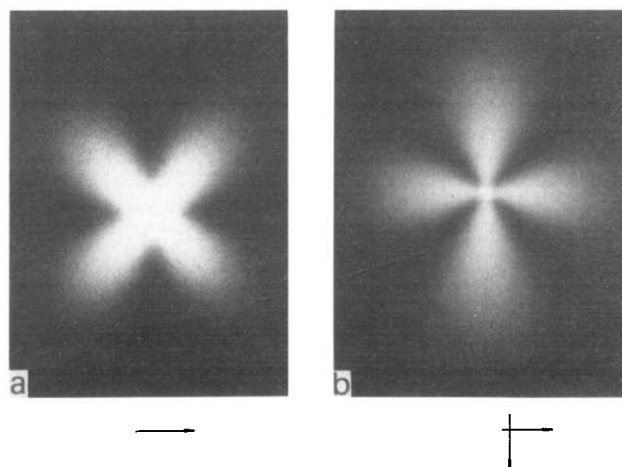


Figure 2 Examples of SALS patterns from crystalline PVK: (a) V_V ; (b) H_V . Arrows indicate polarization directions

directions. It clearly demonstrates differences in the intensity distributions along both directions, and confirms a two-fold symmetry pattern. Similar investigations show the four-fold symmetry of the V_V pattern (Figure 3a).

One can see that intensity of the patterns decreases with an increase in the scattering angle. This characteristic of the intensity distribution indicates that the scattering elements have the form of rods rather than spherulites^{13,15,16}. The presence of extremely large spherulites could be considered, but this possibility can be excluded, however, after microscopic examination of samples. An example of the structure, as seen under polarizing microscope, is given on Figure 4. It should also be mentioned that there was no evidence of macroscopic

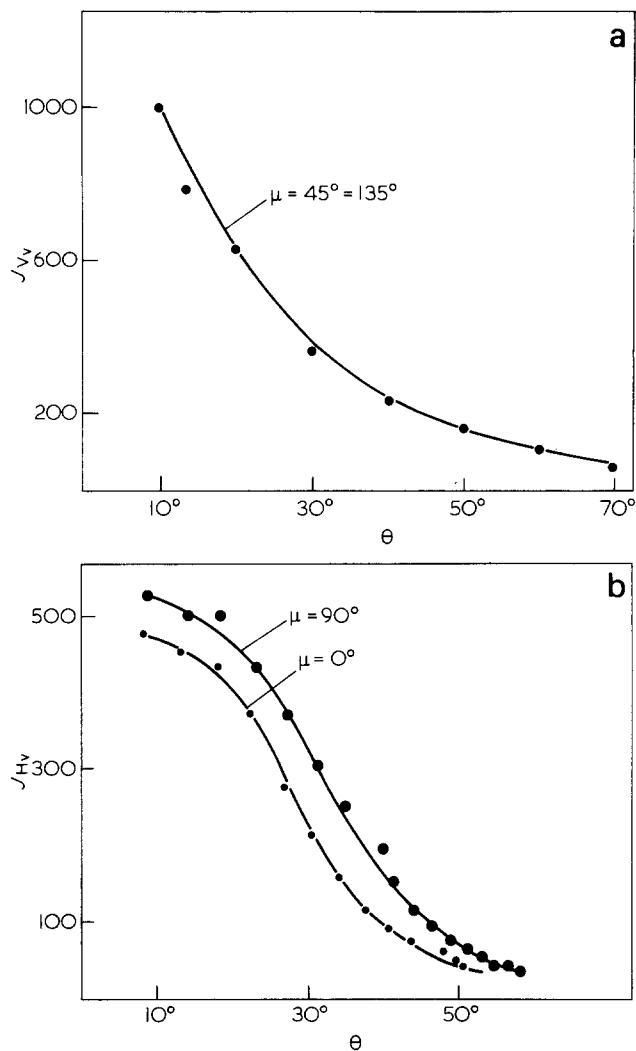


Figure 3 Photometric traces from SALS photographs of PVK: (a) V_V , along azimuthal direction $\mu = 45^\circ$ and 135° ; (b) H_V , along azimuthal direction $\mu = 0^\circ$ and 90°



Figure 4 Morphology of crystalline PVK sample as seen under optical microscope (x320)

orientation from observations under polarizing microscope. Therefore the two-fold symmetry of the scattering pattern has to be associated with other structural features.

It seems that correlation of orientations of elements occurring at some distance between themselves might be responsible for the observed scattering. Theoretical analysis of such a situation was given by Stein *et al.*¹⁷

Using this theory one may attempt to describe the actual situation occurring in the system investigated. According to Stein *et al.*¹⁷ the intensity scattered by system of elements having nonrandom orientation fluctuations can be expressed as a sum of terms (equations (1) and (2)).

$$I_{\parallel} = KE_0^2 \{ \delta^2 [A_1 K_1 + A_2 K_2 + A_3 K_3 + A_4 K_4 + A_5 K_5 + A_6 K_6] + A_7 K_7 \} \quad (1)$$

where:

$$\begin{aligned} A_1 &= \sin^2 \Psi \cos^2 \Psi \\ A_2 &= \sin^2 \Psi \cos^2 \Psi \cos^2 \Theta \\ A_3 &= 2 \sin^2 \Psi \cos^2 \Psi \cos \Theta \\ A_4 &= (\cos^2 \Psi \cos \Theta - \sin^2 \Psi)^2 \\ A_5 &= 2(\cos^2 \Psi \cos \Theta - \sin^2 \Psi) \sin \Psi \cos \Psi \\ A_6 &= 2(\cos^2 \Psi \cos \Theta - \sin^2 \Psi) \sin \Psi \cos \Psi \cos \Theta \\ A_7 &= \sin^2 \Psi \cos^2 \Psi (1 - \cos \Theta)^2 \end{aligned}$$

$$I_{\perp} = KE_0^2 \{ \delta^2 [B_1 K_1 + B_2 K_2 + B_3 K_3 + B_4 K_4 + B_5 K_5 + B_6 K_6] + B_7 K_7 \} \quad (2)$$

where:

$$\begin{aligned} B_1 &= \cos^4 \Psi \\ B_2 &= \sin^4 \Psi \cos^2 \Theta \\ B_3 &= 2 \sin^2 \Psi \cos^2 \Psi \cos \Theta \\ B_4 &= \sin^2 \Psi \cos^2 \Psi (1 + \cos \Theta)^2 \\ B_5 &= 2 \cos^3 \Psi \sin \Psi (1 + \cos \Theta) \\ B_6 &= 2 \sin^3 \Psi \cos \Psi \cos \Theta (1 + \cos \Theta) \\ B_7 &= (\cos^2 \Psi + \sin^2 \Psi \cos \Theta)^2 \end{aligned}$$

In both equations the intensity is expressed as a number of correlation functions K_i , each one being multiplied by the corresponding coefficient A_i in the case of H_V scattering of B_i in the case of V_V scattering. The azimuthal dependence of the scattered intensity is described completely by means of the coefficients A_i and B_i . Since these coefficients are also dependent upon the scattering angle Θ , it becomes clear that the azimuthal distribution of the scattered intensity should change with scattering angle. Figures 5 and 6 show the dependences of coefficients A_i and B_i upon the azimuthal angle Ψ . Various coefficients show very different azimuthal dependences. The final intensity distribution is therefore determined by the coefficients corresponding to most predominant correlation functions K_i .

Examining the dependences shown in Figure 5 one finds that A_4 is the only coefficient which would explain the two-fold symmetry of the H_V pattern, because the value corresponding to the azimuthal angle equal 0° is different to the value of A_4 at 90° . Since the remaining coefficients A_i are very different and their contribution would change the pattern drastically, this means that practically all the correlation functions except K_4 should be negligible. This also means that in the case of the V_V pattern the scattering should be described mainly by the same correlation function. As is seen in Figure 6, the corresponding coefficient B_4 shows its maximum at an azimuthal angle equal to 45° , and it is symmetrical with respect to this direction. The dependence on the azimuthal angle by both coefficients (A_4, B_4) remains in qualitative agreement with the shapes of the H_V and V_V patterns shown in Figure 2. This also confirms the hypothesis that the function K_4 is mainly responsible for the scattering observed in this case.

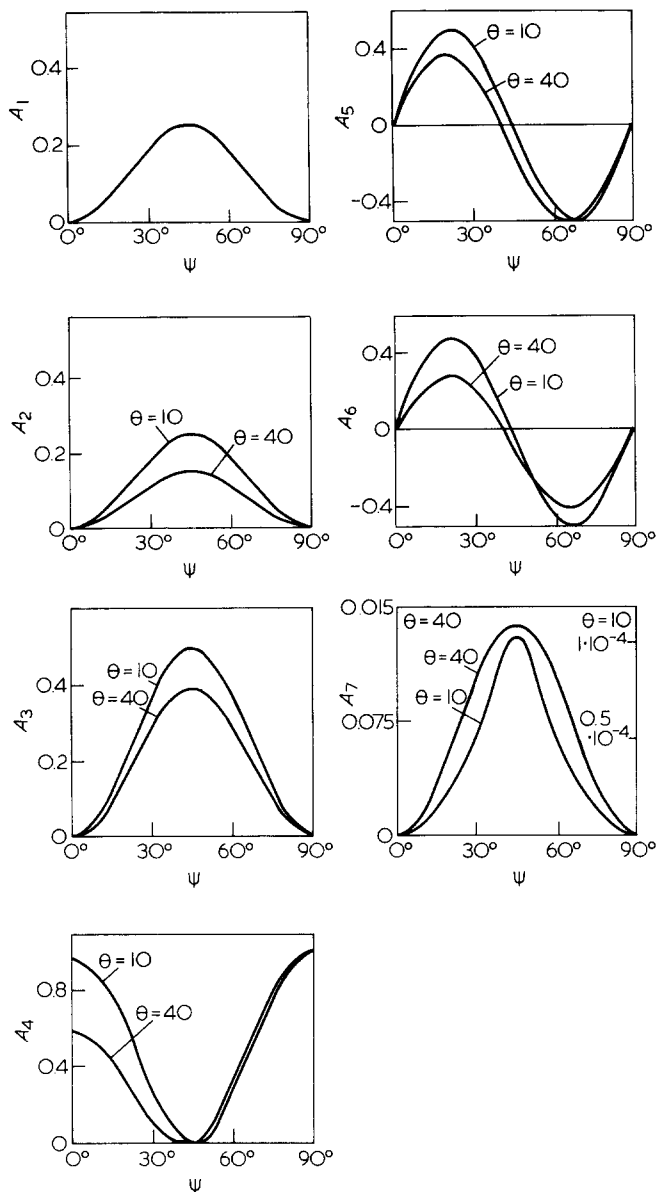


Figure 5 Angular dependence of coefficients A_i defined in equation (1)

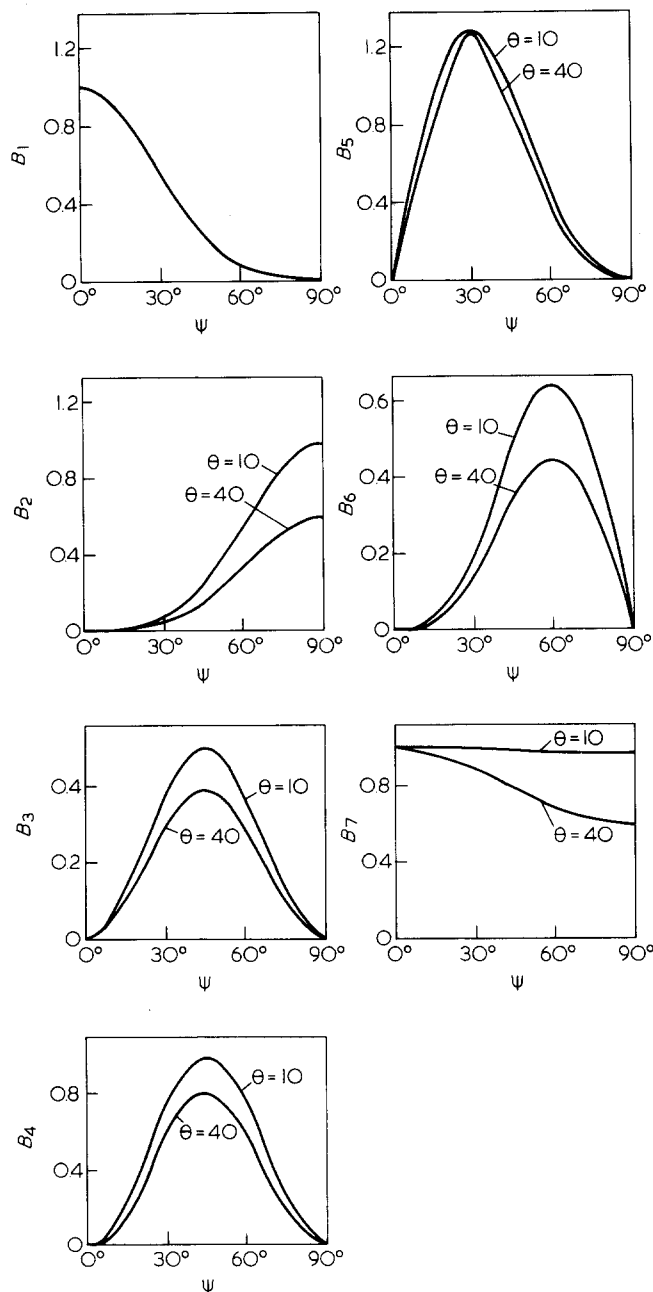


Figure 6 Angular dependence of coefficients B_i defined in equation (2)

Analysis of the behaviour of the equations defining the correlation functions K_4 shows that each function describes a very specific arrangement of scattering centres. Pictures illustrating the character of such arrangements, corresponding to the maximum of each correlation function, are given in Figure 7. As was pointed out, the symmetry of the scattering pattern indicates that function K_4 should predominate over the others in the system investigated here. This means that rod-like scattering elements are correlated in such a way that a number of rods each parallel to the other and tilted at 45° with respect to polarization plane of the incident light always exists. The structure is macroscopically isotropic which means that there are also other series of parallel rods oriented in various directions. During rotation of the sample with respect to the polarization plane, the same number of series of rods always appears in the position tilted at 45° , so the scattering pattern remains unchanged.

CONCLUSIONS

Light scattering studies of PVK samples crystallized under various conditions have shown:

(i) The structure of PVK crystallized at various temperatures from amorphous samples cast from different solvents, appears to be independent of crystallization conditions.

(ii) Characteristics of the SALS patterns indicates the presence of rod-like scattering elements and the existence of nonrandom orientation correlations in the system.

(iii) The correlation in the system consists of a number of parallel rods tilted at 45° with respect to polarization plane. Series of such rods are oriented randomly in various directions to assure macroscopic isotropy of the sample.

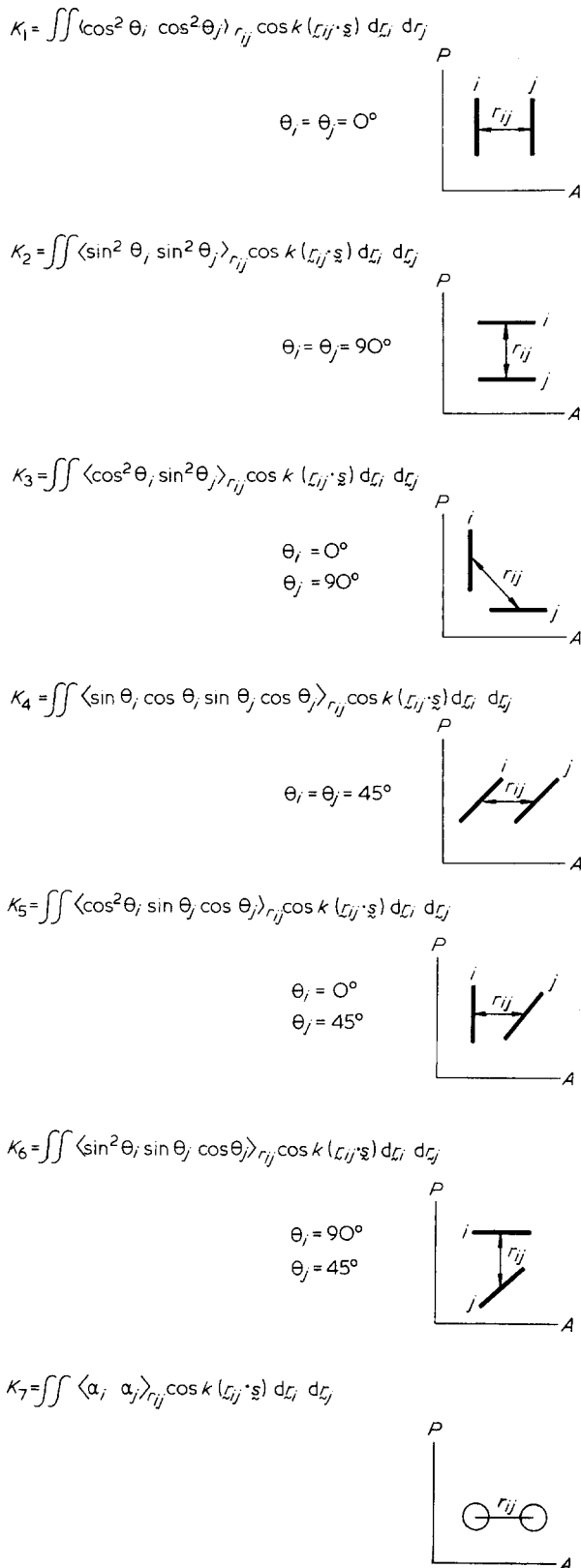


Figure 7 Correlation functions for various types of nonrandom orientation of rods and schematic diagrams of corresponding arrangements

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