Blends of Shape-Persistent Polymers in the Form of Monolayers: Evaluation of the Interaction Parameter†

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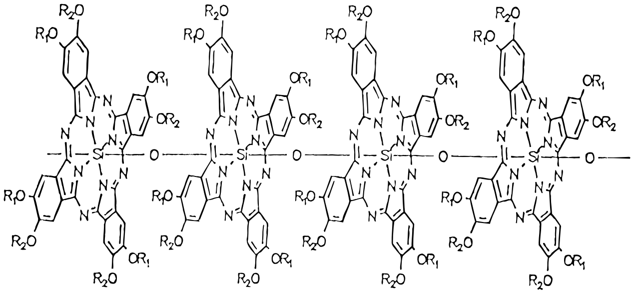
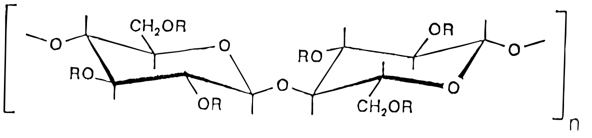
Received October 3, 1995
Revised Manuscript Received December 11, 1995

In a previous communication[1] we have reported that individual shape-persistent synthetic macromolecules can be imaged by transmission electron microscopy (TEM) of monolayers. We have pointed out that mutual interactions between molecules of the same and of different chemical identities lead to nonperiodic structures of aggregates, that is, bundles of the chains differing in aggregation number.

The aim of this communication is to evaluate micrographs of mixtures of (tetramethoxytetraoctoxyphthalocyaninato)poly(siloxane) (PcPS) and isopentyl cellulose (IPC). Both polymers have been shown to give dense and pinhole-free monomolecular films if spread to the air−water interface of a Langmuir trough from a common solvent. By compression and transfer of these films to solid substrates Langmuir−Blodgett (LB) multilayered films are readily constructed.



PcPS (R₁=-CH₃, R₂=-(CH₂)₇CH₃)



IPC (R=-(CH₂)₂CH(CH₃)₂)

Figure 1 shows a TEM micrograph obtained by direct imaging of a single monolayer of a 1:1 by weight mixture of PcPS/IPC, situated on a 5 nm thick carbon film as the support. The film was transferred from the Langmuir trough by the LB technique to the substrate (see Experimental Section) with care taken to avoid or at least minimize mechanical deformation of the texture. Analyzing the pattern, we assume that there are two kinds of objects (**1** and **2**). The objects are considered as extended cylindrical molecules arranged parallel to each other and assumed to be positioned in a random arrangement normal to their axes, for example,

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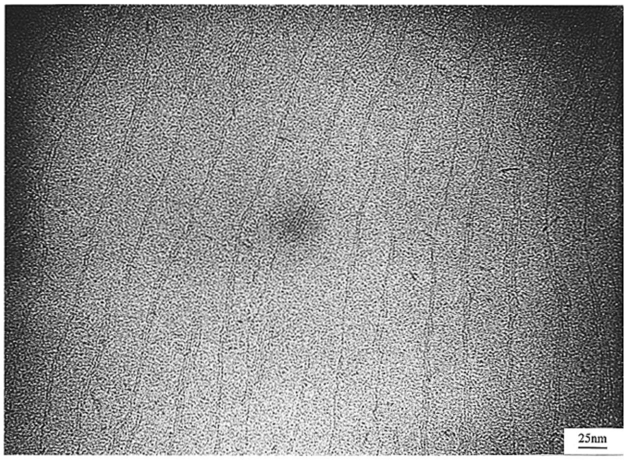

Figure 1. High-resolution TEM image showing the texture of a monolayer of a blend of PcPS/IPC (1:1 by weight). The dark lines represent the chains of PcPS, with a size of ca. 2.25 nm in cross-section. They are embedded in the chains of IPC which have no contrast to TEM.[1]

Further, we assume that N_1 and N_2 are the numbers of the objects **1** and **2**, respectively, at a total number $N = N_1 + N_2$. Clearly, the coordination number equals 2 for the present case. The numbers of the pairs N_{11}, N_{22}, and N_{12} are related to N_1 and N_2 as follows:

$$2N_1 = 2N_{11} + N_{12} \tag{1.1}$$

$$2N_2 = 2N_{22} + N_{12} \tag{1.2}$$

The Hamiltonian is

$$H = N_{11}w_{11} + N_{22}w_{22} + N_{12}w_{12} = N_1w_{11} + N_2w_{22} + \left(w_{12} - \frac{w_{11} + w_{22}}{2}\right)N_{12} \tag{2}$$

where w_{11}, w_{22}, and w_{12} are the interaction energies per contact of interacting units for pairs **11**, **22**, and **12**. The interchange energy w is defined as

$$w = w_{12} - \frac{w_{11} + w_{22}}{2} \tag{3}$$

These interaction energies include all interactions of the pairs with the subphase and the gas phase. In this context we do not intend to separate the terms into the components.

The numbers of the configurations g_1 and g_2 for object contacts are given by

$$g_1 = \left[\left(N_1 - \frac{N_{12}}{2}\right) + \frac{N_{12}}{2}\right]!\Big/\left[\left(N_1 - \frac{N_{12}}{2}\right)!\left(\frac{N_{12}}{2}\right)!\right] \tag{4.1}$$

$$g_2 = \left[\left(N_2 - \frac{N_{12}}{2}\right) + \frac{N_{12}}{2}\right]!\Big/\left[\left(N_2 - \frac{N_{12}}{2}\right)!\left(\frac{N_{12}}{2}\right)!\right] \tag{4.2}$$

and the partition function $Z(N_1,N_2,N_{12})$ by

$$Z(N_1,N_2,N_{12}) = \sum_{N_{12}} g_1g_2 \exp(-H/kT) \tag{5}$$

Maximization of $Z(N_1,N_2,N_{12})$ with respect to N_{12} involves the condition

$$\partial \ln Z(N_1,N_2,N_{12})/\partial N_{12} = 0 \tag{6.1}$$

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† Dedicated to Professor W. Borchard, Universität Duisburg, on the occasion of his 60th birthday.

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As a good approximation we consider only the largest term of the sum in eq 5 and thus

$$\partial \ln Z(N_1,N_2,N_{12})/\partial N_{12} \approx \partial \ln[g_1g_2 \exp(-H/kT)]/\partial N_{12} \tag{6.2}$$

and applying Stirling's formula to approximate g_1 and g_2, we are led to

$$\ln g_1 = N_1 \ln N_1 - \left(N_1 - \frac{N_{12}}{2}\right) \ln\left(N_1 - \frac{N_{12}}{2}\right) - \frac{N_{12}}{2} \ln \frac{N_{12}}{2} \tag{6.3a}$$

$$\ln g_2 = N_2 \ln N_2 - \left(N_2 - \frac{N_{12}}{2}\right) \ln\left(N_2 - \frac{N_{12}}{2}\right) - \frac{N_{12}}{2} \ln \frac{N_{12}}{2} \tag{6.3b}$$

which gives the following expression for the equilibrium value N_{12}^*:

$$\exp(2w/kT) = \frac{\left(N_1 - \frac{N_{12}^*}{2}\right)\left(N_2 - \frac{N_{12}^*}{2}\right)}{\left(\frac{N_{12}^*}{2}\right)^2} \tag{7.1}$$

or

$$\exp(\chi) = \frac{(\beta - \alpha)(1 - \beta - \alpha)}{\alpha^2} \tag{7.2}$$

where $\alpha = N_{12}^*/2N$, $\beta = N_1/N$, and $\chi = 2w/kT$. The symbol α stands for the fraction of the contacts involved in heteropairs. The temperature coefficient $\partial\alpha/\partial T$ is expressed by

$$\partial\alpha/\partial T = 2w\alpha^2 \exp(\chi)/[kT^2(1 - 2\alpha + 2\alpha \exp(\chi))] \tag{8}$$

This expression indicates that $\alpha = N_{12}^*/2N$ increases with the temperature if w is positive, which is true for the present system, as will be confirmed later. In other words, we may conclude that the size I of any single bundle decreases with the temperature ($I = {}^1/_2\alpha$).

Defining $f = \beta/\alpha = 2N_1/N_{12}^*$ and inserting into eq 7.2, we have

$$\partial f/\partial\beta = [(f^2 - 1) + \exp(\chi)]/(2f - 2f\beta - 1) \geq 0 \tag{9}$$

The quantity f represents the average size of the bundles involving the species **1** only, and the fraction of such contacts is given by $1/f$.

The width of the average deviation of the size distribution of the bundles can be described by a deviation parameter σ^2, which we define as

$$\sigma^2 = \left(N_1 - \frac{N_{12}^*}{2}\right) \frac{N_1}{N_1 + \frac{N_{12}^*}{2}} \frac{N_2}{N_2 + \frac{N_{12}^*}{2}} \tag{10.1}$$

or

$$\sigma^2 = N\beta(\beta - \alpha)(1 - \beta)/(\alpha + \beta)(1 + \alpha - \beta) \tag{10.2}$$

It is easy to prove using eq 8 that the value of the deviation decreases with increasing temperature.

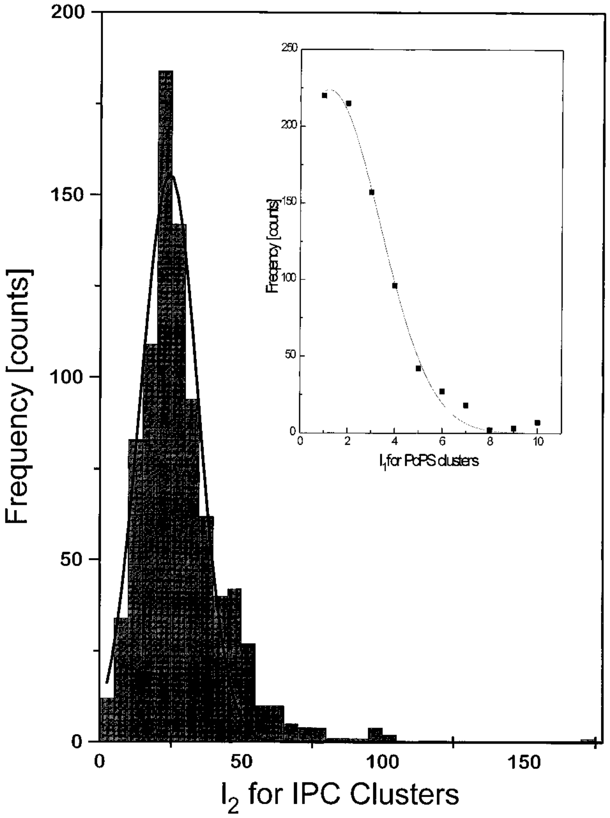

Figure 2. Distributions of the sizes of the clusters of PcPS (I_1) and IPC (I_2) evaluated from a series of TEM micrographs, with the dotted or solid curves showing the respective Gaussian fits. The data refer to monolayers obtained at T = 38 °C; I_1 is in number of PcPS molecules of cross-section diameter 2.25 nm and I_2 is in nanometers.

Table 1. Values of the Parameters from Evaluating the Distributions

T/K	N_1[a]	N_2[a]	N_{12}^*	I_1[a]	I_2[a]	σ_1[a]	σ_2[a]
279	1008	3542	1362	1.55	27.3	4.94	27.4
311	1345	3968	1744	1.22	24.7	4.33	20.2

[a] Indices refer to constituents **1** (PcPS) and **2** (IPC).

Table 2. Parameters Derived from the Data in Table 1

T/K	α	β[a]	χ
279	0.1497	0.2216	0.702
311	0.1641	0.2531	0.655

[a] For PcPS.

Five micrographs like the one in Figure 1 have been evaluated to retrieve the distributions for the two constituents, as shown in Figure 2. The number of chains of PcPS (N_1) was evaluated by a direct count, whereas the number of IPC chains per cluster was evaluated from the distance between each two PcPS clusters divided by the diameter of the IPC chains in the monolayer configuration (1.0 nm)[3]. Fitting these distributions to a Gaussian function as the simplest approach, we obtain the values of the distribution parameters, listed in Table 1, and therefrom, the parameters α, β, and χ are derived. Their values are summarized in Table 2. It is obvious that the theoretical analysis above is supported by these experimental data (Table 1).

In Table 2 we note that the interaction parameter depends on temperature, which implies that the interchange energy has the character of an interchange free energy. Since it is usual to write

$$\chi = a + b/T \tag{11}$$

we find $a = 0.245$ and $b = 127.4K$. The parameter b is related to the interchange enthalpy w_h by

$$w_h = R\frac{b}{2} \tag{12}$$

where R is the gas constant. Thus we find w_h to amount to 127 cal/mol of interacting units, a reasonable value for Van der Waals-type interactions.

A close inspection of many micrographs obtained in the manner described here and elsewhere[1] shows that the clusters of larger and smaller sizes differ with regard to the chain length of PcPS molecules which are aggregated. Furthermore, PcPS clusters close to the core of disclinations[1] seem to consist of shorter chains in order to reduce the local strain exerted onto the shape-persistent molecules in this situation. Such effects were not taken into account in the present analysis and remain to be treated in future work.

Experimental Section. PcPS of $P_n \approx 100$ used here to prepare the specimens for TEM was synthesized as described previously.[2] IPC of $P_n = 150$ and degree of substitution DS = 2.9 was obtained according to Schaub et al.[3] The substrate for film deposition consisted of a thin aluminum foil on top of which a thin carbon film of 5 nm thickness had been evaporated. It was stored in air prior to use for at least 2 h. A Lauda model FW1 Langmuir trough (filled with milli-Q water as the subphase) was used to prepare the monolayers. First the substrate backed by a microscope slide against mechanical distortion was immersed completely into the subphase with the carbon film facing the barrier. A 0.01% by weight solution of a mixture of PcPS and IPC in chloroform (Uvasol, Merck) was then spread onto the subphase. The monolayer of the polymer mixture at the surface was compressed to the desired pressure. The substrate was then lifted vertically through the monolayer to achieve transfer at the constant pressure which was 19 mN/m at 6 °C and 12 mN/m at 38 °C. The transfer ratio was unity. After the sample was dried in nitrogen, the transfer of the film from the supporting substrate onto copper grids for TEM investigation was achieved by dissolving the aluminum foil in dilute hydrochloric acid. The monolayer film on its carbon substrate remained unaffected.

A Philips CM12 transmission electron microscope was used operating at a voltage of 120 kV. The micrograph displayed in this communication is a direct print of the corresponding negative without any image treatment (reduced to 36% for publication).

References and Notes

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(3) Schaub, M.; Fakirov, C.; Schmidt, A.; Lieser, G.; Wenz, G.; Wegner, G.; Albouy, P. A.; Wu, H.; Foster, M. D. *Macromolecules* **1995**, *28*, 1221.

MA951487C