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Magnetic-Field Orientation of the Liquid Crystals of Polyribonucleotide Complexes

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Small-angle laser light scattering and double refractive index measurements on the nematic solutions of poly(A)·poly(U) and poly(A)·2poly(U) have been carried out in static magnetic fields and the data have been discussed in terms of alignment of rodlike molecular clusters having induced, magnetic dipole moments. It has been suggested that these polyribonucleotide complexes are diamagnetic and their maximum magnetic susceptibilities are in the direction parallel to the axes of polymer helices. Best agreement with the measurements is obtained assuming that certain wall effects of the optical cell and spacer, which is introduced into the optical cell, are involved.

INTRODUCTION

Double-stranded helices of poly(A)·poly(U), poly(G)·poly(C) and poly(C)·poly(I) and triple-stranded helices of poly(A)·2poly(U) and poly(A)·2poly(I) in concentrated solutions form liquid crystals of the nematic type, in which the two complexes of poly(A) and poly(U) are converted on standing from the nematic to the cholesteric type.[1] When in a static magnetic field, the layers of molecular alignment of the cholesteric texture become more stable if they are perpendicular to the direction of magnetic field and become unstable if they are parallel to it.[2] The nematic liquid crystals which are reversed from these cholesteric liquid crystals by shearing stresses can be oriented in a static magnetic field with the axes of polymer helices perpendicular to the direction of magnetic field.[3] These evidence suggest that these polymer helices have an anisotropy of magnetic susceptibility. The purpose of this paper is to report more evidence to clarify the mechanism of magnetic-field orientation of the polyribonucleotide complexes.

EXPERIMENTAL

Potassium salt of polyadenylate (poly(A)) and ammonium salt of polyuridylate (poly(U)) were dissolved in 0.08M NaCl and 0.02M sodium citrate plus citric acid with a pH of 7.0 and mixed up at predetermined ratios to obtain two kinds of polymer complexes, poly(A)·poly(U) and poly(A)·2-poly(U). They are respectively double-stranded, and triple-stranded. The concentrated solutions of these polymer complexes were stored at room temperature for several weeks to insure full growth of the cholesteric liquid crystals, stirred up to break down the cholesteric textures to reproduce the nematic textures, and were then introduced into quartz cells of 1-mm pathlength. A quartz spacer was inserted into each optical cell to shorten the lightpath to about 0.1 mm or less. The nematic solutions were also introduced into handmade celluloid cells 11 × 11 mm inside and were dried up slowly in a magnetic field of 25 kilogausses to obtain oriented polymer films, out of which round films were cut. Preparations of the specimens have been described elsewhere.[1–3]

Each nematic solution was placed, with the surface of the optical cell parallel to the direction of magnetic field, between the poles of an electromagnet. Small-angle light scattering patterns were photographed with a 2-mW He-Ne gas laser as the light source (6328 Å) in static magnetic fields up to 25 kilogausses, and measurements of the birefringence were carried out using a double refractometer. Each oriented film was suspended in a magnetic field of 25 kilogausses with a thin thread attached at its center to observe its behavior.

RESULTS AND DISCUSSION

1 Behavior of magnetically oriented films under a static magnetic field

When the oriented films of poly(A)·poly(U) and poly(A)·2poly(U) are brought close to a static magnetic field (of 25 kilogausses), they are repeled from the field, indicating that the polymer films are diamagnetic. However, they stand still when once placed in an uniform field and appear to have a slight tendency to rotate so that the axes of polymer helices (and the long cluster axes, see the next paragraph) become perpendicular to the direction

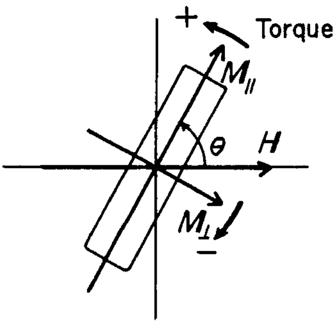

FIGURE 1 Orientation of a diamagnetic rod in a static magnetic field.

of magnetic field. The torque, τ, acting on the rodlike molecular cluster in a static magnetic field (of H gauss) will be given by an equation,

$$\tau = |M_{\parallel} \times H - M_{\perp} \times H| = \tfrac{1}{2}(|\chi_{\parallel}| - |\chi_{\perp}|)H^2 \cdot v \cdot \sin 2\theta \qquad (1)$$

where $M_{\parallel}$ and $M_{\perp}$ are the components of a magnetic dipole induced in the molecular cluster, respectively parallel and perpendicular to the long cluster axis. $\chi_{\parallel}$ and $\chi_{\perp}$ are the magnetic susceptibilities corresponding to $M_{\parallel}$ and $M_{\perp}$, respectively. θ is the angle that the long cluster axis makes with respect to the direction of magnetic field and v is the (mean) volume of molecular cluster (Figure 1). The potential energy of the molecular cluster, U, at any θ will be given in a form,

$$U = -\int \tau d\theta = \tfrac{1}{4}\Delta\chi \cdot H^2 \cdot v \cdot \cos 2\theta, \qquad \Delta\chi \equiv |\chi_{\parallel}| - |\chi_{\perp}|. \qquad (2)$$

If $|\chi_{\parallel}| > |\chi_{\perp}|$, the potential energy becomes minimum at $\theta = 90°$, which explains the behavior of the polymer films in the static magnetic field. Thus, the magnetic susceptibility of the helices of polyribonucleotide complexes is larger in the direction parallel than perpendicular to the polymer helices. Blois and Maling were the first to suggest the presence of an anisotropy of magnetic susceptibility of deoxyribonucleic acid.[4] The anisotropy we have found would be genuine to the polyribonucleotide complexes. However, nucleic acids are very easy to be contaminated with impurities such as transition metals and there have been big arguments concerning whether or not observed magnetic resonance of nucleic acids is genuine to them.[5,6] Thus, the adsorption of metals on the surface of rodlike molecular clusters, if any, might produce (induced) dipoles in these clusters. Although the magnetic-field orientation occurs also when just deionized water is used instead of buffer solvent to prepare solutions, the possibility of metal-adsorption effect may still not completely be ruled out.

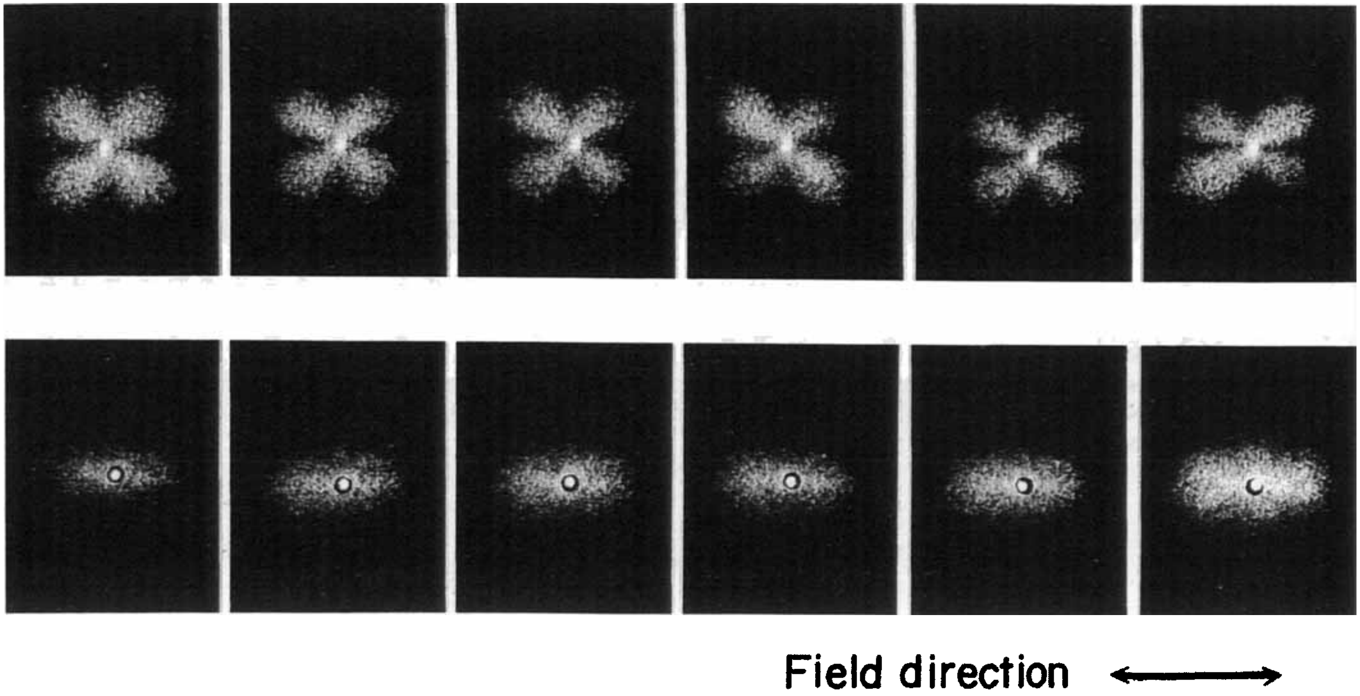

FIGURE 2 Field-strength dependence of the steady-state patterns of the small-angle laser light scattering. Specimen, poly(A) · poly(U)—10.5 vol %. Field strength: from left to right, 0, 10, 16, 20, 23, 25 kilogausses. Upper, H_v patterns and lower, V_v patterns.

2 Small-angle light scattering

The H_v scattering pattern of the nematic solutions of poly(A)·poly(U) and poly(A)·2poly(U) is mostly of the ±45° type, suggesting that each solution is a collection of rodlike molecular assemblies (molecular clusters) whose maximum polarizability directions are either parallel or perpendicular to the long cluster axes.[7] These directions are perpendicular in this case because in each molecular cluster the polymer helices align themselves parallel to the long cluster axis.[1] The right (and the left) angle of intersection of the cross pattern (of ±45° type) decreases starting from 90° with the increase of magnetic-field strength when the field direction is transverse (Figure 2). This suggests that the rodlike molecular clusters align themselves with their long cluster axes perpendicular to the direction of magnetic field.[8–10] At times, the H_v pattern is circular without magnetic field, suggesting that the rodlike molecular clusters are not well separated; however, it turns to be of the ±45° type and follows the same procedure under the influence of magnetic field. The shape of V_v pattern is an ellipse whose long axis is parallel to the direction of magnetic field in accordance with the conclusion derived from the H_v results.[9,10] The V_v pattern is sometimes elliptic even without magnetic field, whereas it should be circular for the random arrangement of rodlike molecular clusters.[9] This would suggest that they are subjected to certain spontaneous orientation probably with respect to the optical cell (and spacer) surface.

3 Birefringence

The refractive index of the oriented nematic solutions of poly(A)·poly(U) and poly(A)·2poly(U) is larger for light whose electric vector is parallel than perpendicular to the direction of magnetic field. This indicates that the polyribonucleotide helices are perpendicular to the field direction because they are known to have negative birefringence.[11] This evidence agrees with the finding concerning the ordering of rodlike molecular clusters (in which the polymer helices align parallel to the long cluster axes) as obtained from the light scattering measurements. The steady-state birefringence of both poly(A)·poly(U) and poly(A)·2poly(U) is proportional to the square of magnetic-field strength except at low field strengths, say 16 kilogausses or less (Figure 3). This experimental evidence can be elucidated as follows.

The nematic solution of polyribonucleotide complexes in magnetic field will be assumed to be a system of rods having induced, magnetic dipole moments. (The orientation of the solution does not change upon reversal

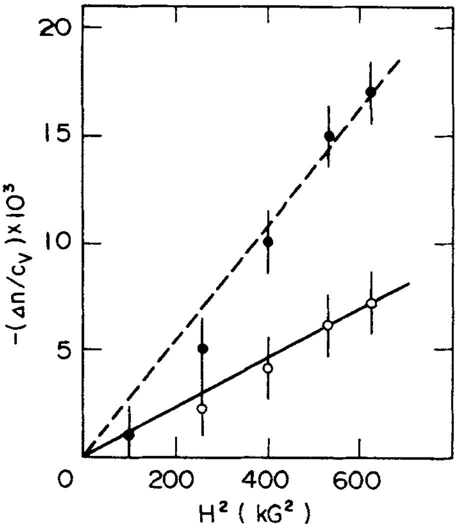

FIGURE 3 Values of the steady-state birefringence as a function of the square of magnetic-field strength. Full line, poly(A)·poly(U)—8.1 vol % and broken line, poly(A)·2poly(U)—10.5 vol %.

of the field direction when the steady-state orientation is attained.) The orientation factor, Φ, of this system is given in the form,[12]

$$\Phi = \tfrac{1}{2}\int_0^{\pi/2}(3\cos^2\theta - 1)\cdot e^{-U/kT}d\Omega \Big/ \int_0^{\pi/2} e^{-U/kT}d\Omega$$

where θ is the tilt angle of rod axis with respect to the position of energy minimum, k is the Boltzmann constant and T is the absolute temperature. U is the potential energy of rod in a static magnetic field (H gauss) and is given by replacing θ with $(\pi/2) - \theta$ in Eq. 2. Substituting x for $\Delta\chi \cdot v \cdot H^2/4kT$ and y for $\cos\theta$ and approximating the exponential function as $1 + x(2y^2 - 1)$ provided that $x \ll 1$, the following result is obtained:

$$\Phi \fallingdotseq 28x/(105 - 35x^2) \fallingdotseq 0.267x = 0.067\Delta\chi\cdot v\cdot H^2/kT \qquad (3)$$

This result predicts that the orientation factor is proportional to the square of magnetic field strength. However, it should be noticed that this orientation factor is calculated with respect to the rod axes which are perpendicular to the "long" rod axes. Considering the random orientation of rods around the axis parallel to the direction of magnetic field, the birefringence of the system will be given by the following expression,

$$\Delta n/c_v = \tfrac{1}{2}(\Delta n/c_v)_0\cdot\Phi \qquad (4)$$

where Δn is the double refractive index of the oriented solution and c_v is the volume fraction of rods. $(\Delta n/c_v)_0$ is the birefringence at perfect orientation and is about 0.1.[11] At any rate, the birefringence is known to be proportional to the square of magnetic field strength. Although the condition that $x \ll 1$ is not fully satisfied, the experimental evidence is now explained. The result that the birefringence is lower than expected at low field strengths is considered to be due to some wall effects arising from the inner surface of the optical cell and spacer surface as will be mentioned shortly.

The decay of birefringence of the oriented nematic solutions of poly(A)·poly(U) and poly(A)·2poly(U) after removal of the external, magnetic field (of 25 kilogausses) is well expressed by the sum of two exponential components (Figure 4),

$$\Delta n/c_v = (\Delta n/c_v)_{t=0}[C \cdot e^{-1/\tau_1} + (1 - C) \cdot e^{-t/\tau_2}] \tag{5}$$

where τ_1 and τ_2 are relaxation times and C is a constant having a value between 0 and 1. Examples of the numerical results are shown in Table I. The first term in Eq. 5 decays more than 5 times faster than the second and is considered to be related to some wall effects by which the rodlike molecular clusters are forced to be rearranged in some specific manner with respect to the surface of the optical cell and of the spacer as in the case of the liquid crystals of poly(γ-benzyl-L-glutamate).[8,13] Each spacer which was inserted into the optical cell made contact with either inner surface of the optical cell. Judging from the values of C and solution thickness, the limit of range (coherent length) in which the rodlike molecular clusters are under the influence of walls is estimated to be about 10 μm from them. The second term

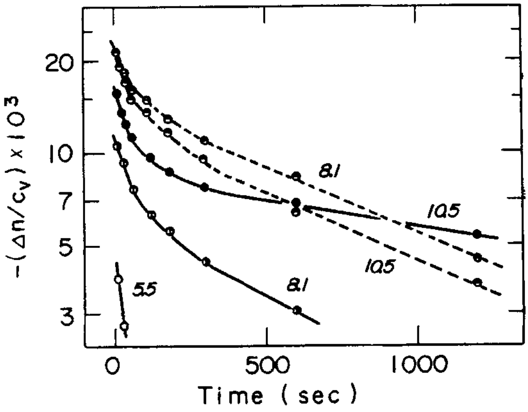

FIGURE 4 Logarithmic plot of the birefringence against time after removal of the magnetic field (of 25 kilogausses). Full lines, poly(A)·poly(U) and broken lines, poly(A)·2poly(U). Numbers on the lines represent the polymer concentration in vol %.

TABLE I

Decay of the birefringence of the magnetically oriented solutions after removal of the magnetic field

Substance	Polym. concn. (vol. %)	τ_1 (sec)	τ_2 (sec)	Θ ($\times 10^{-4}$ sec^{-1})	C	Thickness (μm)
poly(A)·poly(U)	8.1	140	770	2.16	0.45	98
	10.5	135	2530	0.66	0.51	33
poly(A)·2poly(U)	8.1	205	1030	1.62	0.38	58
	10.5	190	1010	1.65	0.40	58

The measurements were carried out at 20°C. See the text.

is considered to be free from the wall effects. The value of apparent rotational diffusion constant, Θ, of the rodlike molecular cluster as calculated by the relation, $\Theta = 1/6\tau_2$, has the order of 10^{-4} sec^{-1}.

CONCLUSION

In summary, the magnetic-field orientation of nematic liquid crystals of poly(A)·poly(U) and poly(A)·2poly(U) appears to be caused by the anisotropy of magnetic susceptibility induced in the rodlike molecular clusters which form the liquid crystals. Parts of the molecular clusters in solution are under the influence of wall effects which are overcome by the magnetic-field effects at high magnetic-field strengths.

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