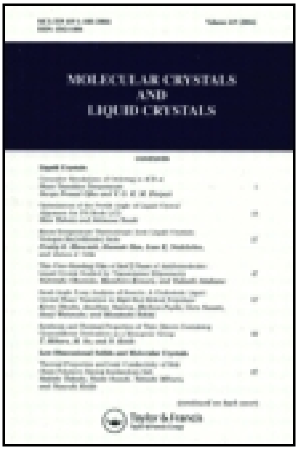

Molecular Crystals and Liquid Crystals

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Experimental Investigations of the Conditions for the Formation of the Liquid Crystalline State of Polymers

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Experimental Investigations of the Conditions for the Formation of the Liquid Crystalline State of Polymers

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The diagrams of state for concentrated PBG solutions in coordinates relating volume fraction—geometric asymmetry and volume fraction—temperature are investigated. The order parameter for macromolecules in the anisotropic phase is determined. The experimental data compare with the existing theoretical models for the formation of the liquid crystalline state in solutions of stiff polymer molecule. It is shown that experimental data are in good quantitative agreement with the Flory's lattice model.

INTRODUCTION

In recent years great attention has been paid to investigations of general factors relating to the formation of the liquid crystalline state of polymers, because new, stiff polymers and polymers with mesogenic groups in both the main and the side chains have been synthesized.[1] As a rule, stiff polymers melt above the temperature of their degradation, and the liquid crystalline state for these polymers was observed only with solutions. Polymers with mesogenic groups in the backbone and in the side chains are considered to be thermotropic liquid crystalline systems, with the exception of comblike polymers[2] forming "liquid crystals" on the level of a single molecule. It may be considered that the general laws of formation of the liquid crystalline state are similar for both lyotropic and thermotropic systems, whereas the geometric asymmetry of the whole macromolecule or its parts is an important parameter for formation of the liquid crystalline state. The dependence of the conditions for formation of the liquid crystalline state on the asymmetry of the macromolecule is more evident in the case of lyotropic liquid crystals formed by stiff polymers. Recently some theoretical models for the formation of the liquid crystalline state in a system of very anisotropic particles have been developed.[3-5] Although the physical principles of these models are different, the theoretical diagrams for the state of a system formed by anisotropic particles are qualitatively similar. The correctness of the theoretical models of the formation of the liquid crystalline state can be checked experimentally. Corresponding data are known for two classes of polymer: polypeptides (poly-γ-benzyl-L-glutamate, PBG[6] and poly-ε-carbobenzoxy-L-lysine, PCBL[7]) and aromatic polyamides: poly-*p*-benzamide, PBA and poly-*p*-terephthalamide, PTA.[8] However, correct quantitative comparison of experimental and theoretical data is evidently possible only for polypeptides, since in the case of polyamides, considerable discrepancies in the values of their geometric asymmetry are observed.[9] The experimental data on phase coexistence are usually compared with Flory's theoretical data[3] for a lattice model of the formation of the liquid crystalline state. These data are qualitatively similar, but exhibit considerable quantitative deviations. First there are the divergences between the experimental and theoretical results concerning the dependencies of concentration boundaries of coexisting phases on the asymmetry of the macromolecules; secondly, the temperature dependence of concentration boundaries for narrow biphasic regions obtained experimentally is quite different from the theoretical dependence. These deviations may be due to the fact that the approximations made in the lattice model are rough, or that experimental errors arise in the determination of the concentrations for the transition to the liquid crystalline state. Finally, these deviations may be due to errors in the determination of the χ parameter and the geometric asymmetry of the macromolecules. These parameters are of great importance in Flory's theory.[3]

This paper is an experimental attempt to consider some factors responsible for these discrepancies.

EXPERIMENTAL

Unfractionated† samples of PBG (mol.w. 50000–450000) were prepared by the condensation of the *N*-carboxyanhydride in benzene with triethylamine as initiator. Methylene chloride (MC), chloroform (CH), dioxan (DO), dimethylformamide (DMF), and trifluoroacetic acid (TFA) used as solvents were distilled and purified before use. Samples were solvated in tubes 5 mm diameter for 7 to 15 days. IR spectra were recorded with a UR-20 spectrometer. The formation of the liquid crystalline state was examined using a polarizing microscope.

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† The polydispersity of the samples is $M_w/M_n = 1.2$.

RESULTS AND DISCUSSION

The theoretical dependence of the concentration boundary of transition to the liquid crystalline state on geometric asymmetry determined by Flory's equation,

$$\ln(1 - V_2) - P^{-1}\ln V_2 = \ln(1 - V_2') - P^{-1}\ln V_2' - \ln[1 - V_2'(1 - y^{-}/P)] + P^{-1}\ln f \quad (1)$$

where V_2 is the concentration at the transition to the liquid crystalline state, P is the geometric asymmetry of macromolecule is shown in Figure 1 for the lattice model (athermic conditions). Similar experimental dependencies for PBG—MC, PBG—CH, PBG—DMF systems are shown in the same figure. It is clear that considerable quantitative divergencies between the theoretical and experimental results exist. Marked deviations in the values of the transition concentrations for different solvents are also observed, in particular at low values of geometric asymmetry (range of low mol.w.) For geometric

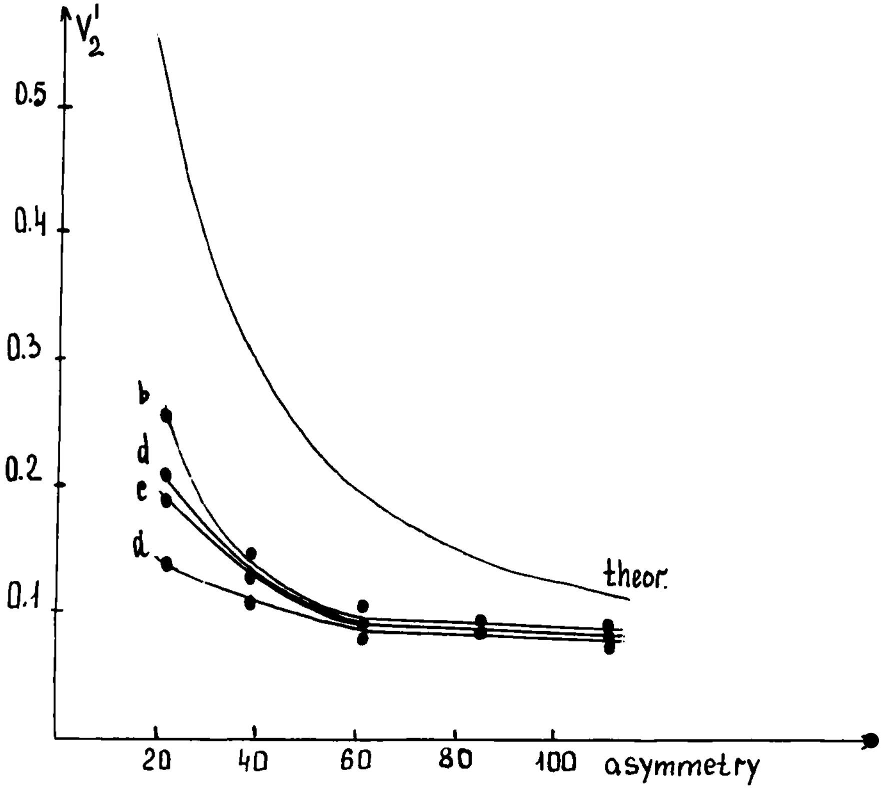

FIGURE 1 The theoretical[3] and experimental dependencies of the concentration boundaries of the transition to liquid crystalline state on geometric asymmetry for the systems: a) PBG—MC, b) PBG—CH, c) PBG—DO, d) PBG—DMF.

asymmetry we used either the values determined for dilute solutions of PBG[10] or those calculated by using a) the equation $P = L/d$, assuming that the molecules of PBG are rodlike or b) the equation from[11]

$$P = a/d[2(L/a - 1 + e^{-L/a})]^{1/2} \tag{2}$$

where L is the contour length of the molecule, a is the persistent length, and d is the thickness of the molecule (15.5 Å for PBG). In the case b) the PBG molecule is assumed to have the shape of a persistent chain for the range of low mol.w.

The question arises whether the use of the values of geometric asymmetry calculated for dilute solutions is correct for concentrated solutions. One of the reasons for this incorrectness may be an aggregation of the PBG molecules in solvents such as DO or CH. The aggregation phenomenon is known to be absent in dilute solutions of PBG in DMF,[12] but nothing is known about the properties of DMF in concentrated solutions of PBG. Thus, for a correct comparison of the theoretical and experimental data on boundaries of transition it is necessary to use non-aggregated solutions. TFA is known to be a very strong non-aggregating solvent[13] which can even cause the helix-coil transition in polypeptides. The results on the effect of the addition of TFA (2%) to liquid crystalline solutions of PBG of different mol.w. are shown in Table I. In some cases the transition to the biphasic or isotropic state takes place. This change in the phase state of the system is probably due to the dissociation of the aggregates of the PBG molecules by TFA (a very low content of TFA does not lead to a conformational transition in the PBG macromolecules). It is known that as the concentration of polypeptides in solution increases, the content of acid ensuring the conformational transition should also be increased. Therefore it may be expected that the content of acid required for the dissociation of aggregates should also be increased. It is of great importance to

TABLE I

Effect of low concentrations of TFA (2%) on the liquid crystalline state of PBG solutions in methylene chloride

	Concentration of PBG in solution		
Mol.w. $\times 10^{-3}$	Critical conc.	2% larger than the critic. conc.	5% larger than the critic. con.
55	"–"	"–"	"–"
80	"–"	"–"	biphasic
100	"–"	"–"	biphasic
170	"–"	"–"	biphasic
250	"–"	"+"	"+"
350	"–"	"+"	"+"
450	"–"	"+"	"+"

Note: "–" is an isotropic solution.
"+" is a liquid crystalline phase.

find the criteria for the existence of non-aggregated PBG molecules in liquid crystalline solution, since the existence of partly non-aggregated molecules may be the reason for considerable changes in the concentration boundaries of the coexisting phases. Since the content of acid for the helix-coil transition in dilute solutions of PBG is far from that needed for the dissociation of aggregates, it may be supposed that all aggregates are dissociated near the conformational transition point.

The procedures used to study conformational transitions in polypeptides (such as DOR and NMR[14–16]) are not used for concentrated solutions. Hence, the method of IR spectroscopy was used for conformational investigations. It was shown that the conformational transition is weakly dependent on the mol.w. of the polymers, as has been shown for dilute solutions.[13] The dependence of the beginning of the conformational transition on the concentration of the polymer for the system of MC—TFA is shown in Figure 2. The scheme for the determination of the concentration boundary of transition to the liquid crystalline state in a mixed solvent (MC—TFA) is shown in Figure 3. The

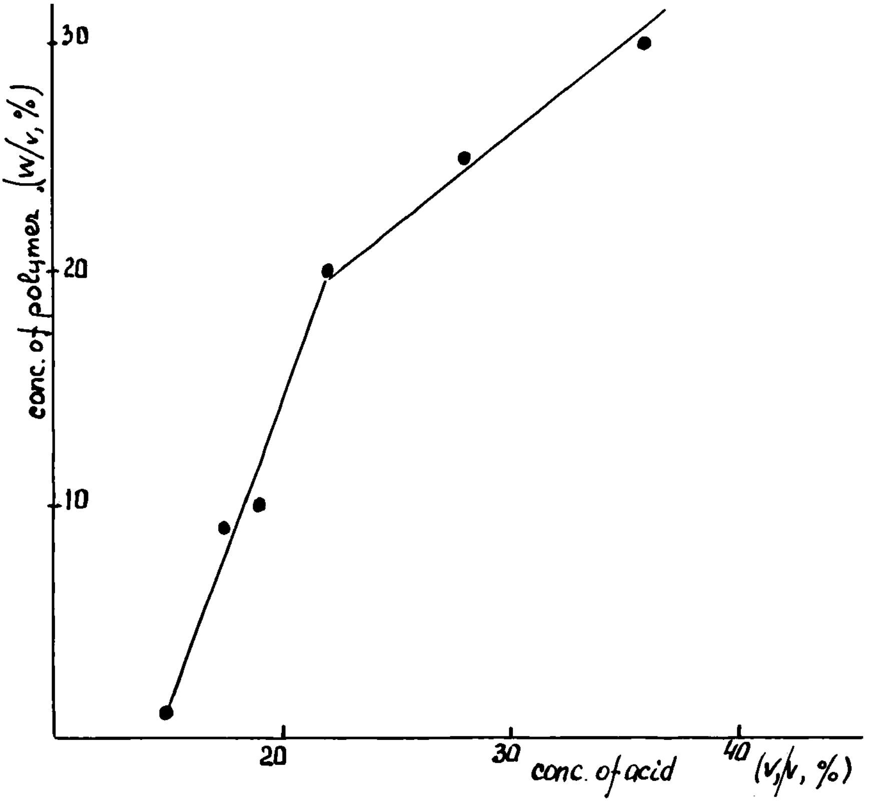

FIGURE 2 The dependence of the beginning of conformational transition on the concentration of PBG in solution.

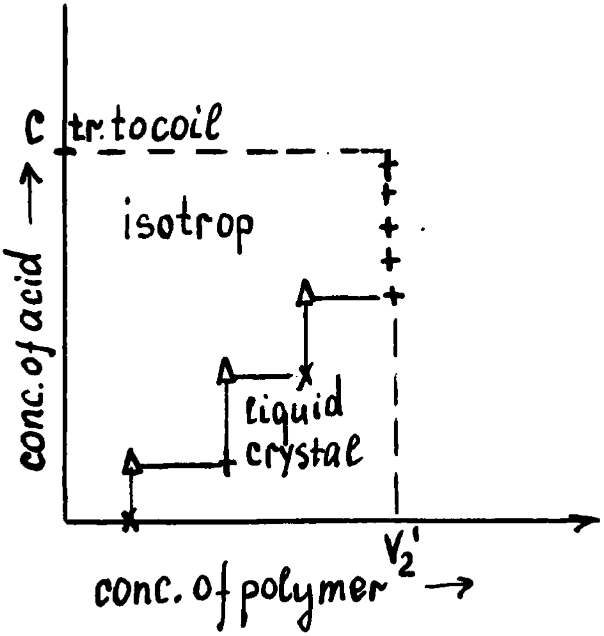

FIGURE 3 The scheme for the determination of the concentration boundaries of the transition to the liquid crystalline state.

value obtained greatly differs from that in a PBG—MC solution. It is evident that there is a limiting concentration of the polymer for a given mol.w. at which the liquid crystalline state exists over the entire range of the TFA content before the conformational transition. Hence, this concentration of the polymer corresponds to an absence of aggregates in solution. This is also confirmed by good agreement between the values for the geometric asymmetry of PBG molecules of different mol.w. in different mixed solvents containing TFA under conditions in which aggregates are absent. The dependence of V_2' on the geometric asymmetry of the macromolecules for the PBG—MC—TFA system is shown in Figure 4. The same figure shows a similar theoretical dependence for the lattice model for a) "the assumption of 1956"[3] and b) the "results of 1979."[17] It is evident that the theoretical (particularly that of 1979[17]) and experimental curves are in good agreement in the range where the PBG molecule may be regarded approximately by a rigid rod. In the range of mol.w. 170000–450000, where a partial deviation in the shape of the molecules from that of a rod is observed, the theoretical and experimental dependencies differ slightly, but these differences exceed experimental errors. This may be due to the impossibility of the use of Eq. (2) for polymers whose shape differs greatly from that of a rod. The satisfactory agreement between the theoretical and experimental dependencies of V_2' on asymmetry is evidence in favor of the lat-

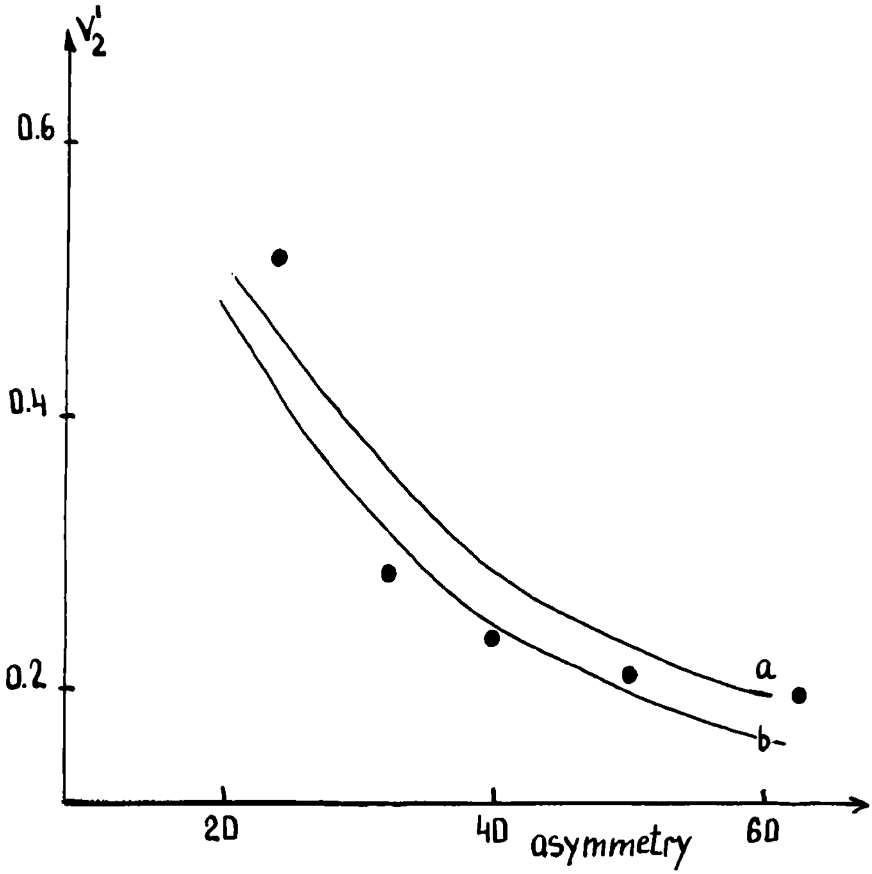

FIGURE 4 The dependence of V_2' on geometric asymmetry under non-aggregated conditions: theoretical data 1956-a), 1979-b), experimental data—●.

tice model for describing the liquid crystalline state in polymers. On the other hand, this agreement is also confirmation of the uniform distribution of solvent and PBG molecules in the liquid crystalline solutions as suggested previously.[18]

Let us consider the biphasic range of the phase diagram. The theoretical and experimental dependencies of V_2 on the geometric asymmetry of the solute molecules are shown in Figure 5. Experimental dependencies of V_2 on geometric asymmetry are shown for the PBG—MC, PBG—DO, PBG—CH, PBG—DMF, and PBG—MC—TFA systems. The values of V_2 were determined using a polarizing microscope. "True," non-aggregated solutions in mixed solvents were obtained by the procedure described before. The concentration 1% lower than that at which the biphasic system exists up to the beginning of

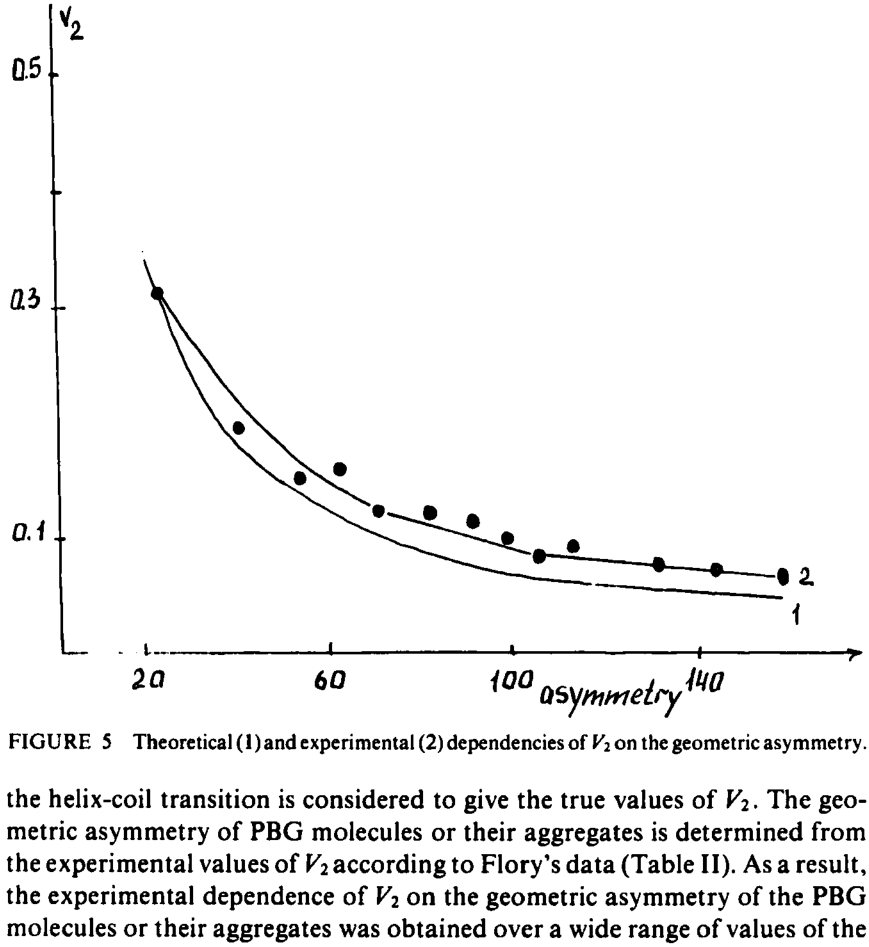

FIGURE 5 Theoretical (1) and experimental (2) dependencies of V_2 on the geometric asymmetry.

the helix-coil transition is considered to give the true values of V_2. The geometric asymmetry of PBG molecules or their aggregates is determined from the experimental values of V_2 according to Flory's data (Table II). As a result, the experimental dependence of V_2 on the geometric asymmetry of the PBG molecules or their aggregates was obtained over a wide range of values of the geometric asymmetry (from 20 to 150). It is evident that the theoretical and experimental curves are similar. However, the observed differences between the experimental and theoretical values of V_2 are greater than the similar differences for V_2'. This may be due to some uncertainty in the determination of the experimental boundary of V_2 as a result of the "subjectivity" of the estimation of this boundary employing a polarizing microscope. It should be noted that the experimental values of V_2'/V_2 and the theoretical values of Flory,[17] Onsager,[4] and Choklov[5] are similar, but the experimental values of PV_2' (see Table III) seem to indicate that the Flory lattice model is the most adequate model for describing the formation of the liquid crystalline state in polymer solutions. It should be noted that the experimental dependencies of V_2 on geometric asymmetry include various systems with various solvents and various nature of the geometric asymmetry of the polymer particles. This is

TABLE II

Values of the geometric asymmetry of PBG aggregates of different molecular weight

Solvent Mol.w. $\times 10^{-3}$	MC	DO	CH	DMF
55	95	67	52	67
80	102	80	78	76
100	112	—	95	—
170	137	137	102	112
250	137	137	137	122
350	154	—	142	122
450	154	—	—	—

MC: methylene chloride.
DO: dioxan.
CH: chloroform.
DMF: dimethylformamide.

further evidence of the fact that, in the case of athermic mixing, only the geometric asymmetry of the polymer particle is responsible for the corresponding phase transitions in solutions of stiff polymers.

Let us consider the temperature dependence of the concentration boundaries of the coexisting phases in the PBG—DMF system. In the case of athermic solutions, the theoretical and experimental data are quite different. The reasons for these differences have been discussed elsewhere.[19] It was shown that (Table IV) solutions of PBG in DMF should not be considered as non-aggregated solutions. It may be supposed that the aggregation of the PBG molecules is the reason for the quantitative and qualitative differences observed in the temperature dependencies of the concentration boundaries of the biphasic

TABLE III

Experimental (for PBG molecules of different geometric asymmetry) and theoretical values of V'_2/V_2 and PV_2

				Theoretical data					
				by Flory				by Onsager	
Experimental data				(Ref 3; 1956)		(Ref 17; 1979)		(Ref 4)	
P	V'_2/V_2	PV_2	P	V'_2/V_2	PV_2	V'_2/V_2	PV_2	V'_2/V_2	PV_2
23	1.31	13.2	20	1.427	10.84	1.367	9.94		
32	1.20	11.76	30	1.527	12.0	1.411	10.0		
80	1.40	12.4	60	1.578	12.0	1.444	10.4		
120	1.40	12.4							
			∞	1.592	13.16	1.465	11.57	1.343	4.486

TABLE IV

Values of V_2, V'_2, and geometric asymmetry P of molecules of PBG in DMF solution and under non-aggregated conditions

Mol.w. $\times 10^{-3}$	Solutions in DMF						Non-aggregated condition[17]		
	$T = 25°$			$V_2 = 0.18$ $T = 120°$					
	V_2	V'_2	P	V_2	V'_2	P	V_2	V'_2	P
120	0.13	0.18	67	0.15	—	—	0.18	0.22	54
200	0.125	0.14	87	0.14	0.17	70	0.15	0.18	67
300	0.11	0.12	100	0.14	0.16	76	0.14	0.16	76

range.† In this case, the increase in temperature may affect the degree of aggregation of the PBG molecules. The dependence of the intrinsic viscosity $[\eta]$ of PBG solutions in DMF on temperature is shown in Figure 6. It is evident that increase in the temperature of solutions whose concentrations are far from V_2 leads to a gradual decrease in the value of $[\eta]$ which approaches that for a dilute solution. Thus temperature may actually be a disaggregating factor. The temperature changes (from 20 to 120°) on V_2 and V'_2 for a biphasic region of the diagram for PBG—DMF systems (mol.w.s of PBG = 120000, 200000, and 300000) were studied using a polarizing microscope (Figure 7). The values of V_2 and V'_2 changed gradually with temperature up to certain concentrations for samples with mol.w. 300000 and 200000, but for PBG of mol.w. = 120000, only the value of V_2 depends on temperature. The values of the geometric asymmetry of the PBG molecules determined at the corresponding temperatures from the values of V'_2 are given in Table II. This table also lists the values of the true geometric asymmetry of these molecules obtained from the data under non-aggregated conditions. It is evident that these values of geometric asymmetry coincide at some temperature, and for samples of mol.w. = 200000 and 300000 further, increase in temperature does not change the values of V_2 and V'_2, and consequently the values of the geometric asymmetry. These data indicate that the observed temperature dependence of the values of V_2 and V'_2 is actually related to the change in the degree of aggregation of the PBG molecules in DMF. It should be noted that the absence of temperature changes on the values of V_2 for PBG of mol.w. = 120000 (corresponding to a concentration of 36–37%) shows that the non-aggregating effect of temperature in the systems discussed depends on the concentration of the polymers. When the concentration of PBG is high, it is impossible to achieve

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† The effect of temperature on the boundaries of the biphasic region could be studied for a PBG-mixed solvent system in which aggregation of the PBG molecules is absent. However, a change in the temperature in this system may lead to changes in the interaction of TFA with PBG, and as a result the situation will be more complicated.

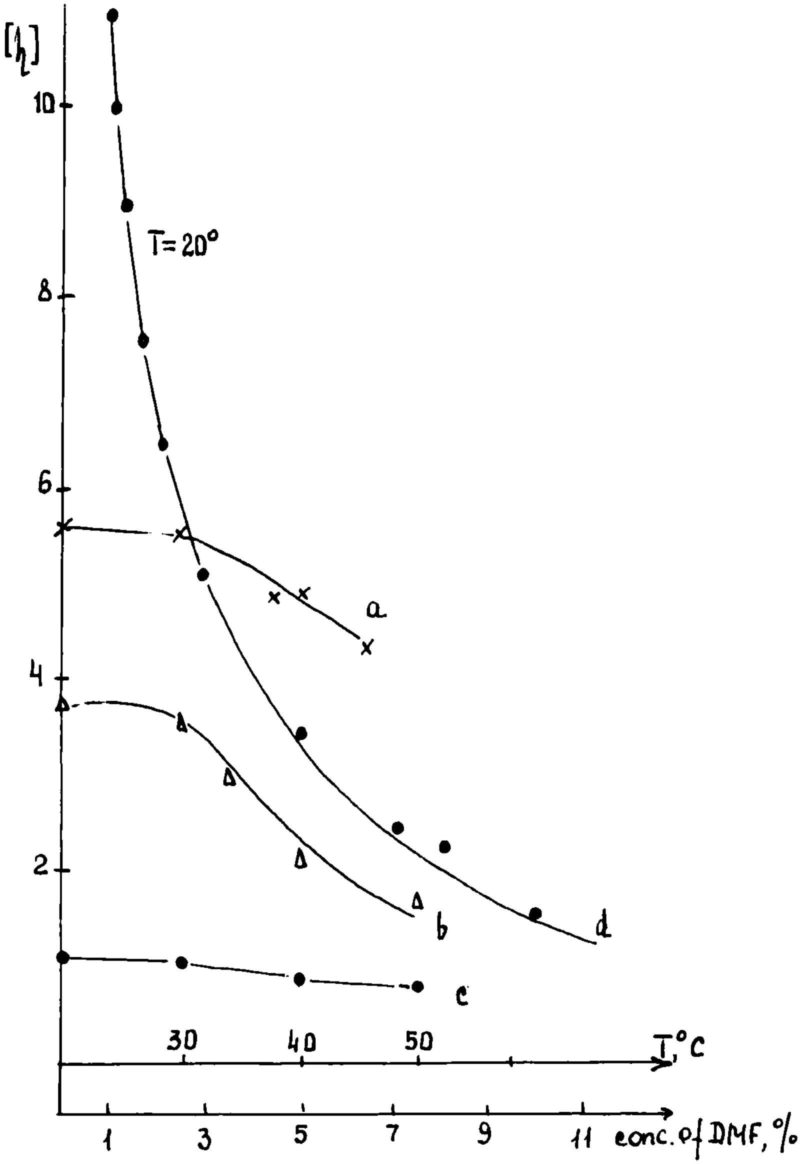

FIGURE 6 The dependence of [η] on the temperature and concentration of DMF (curve d) for dilute solutions of PBG a) PBG in mixed DO—DMF (3%) system; b) PBG in mixed DO—DMF (4%) system; c) PBG in mixed DO—DMF (50%) system.

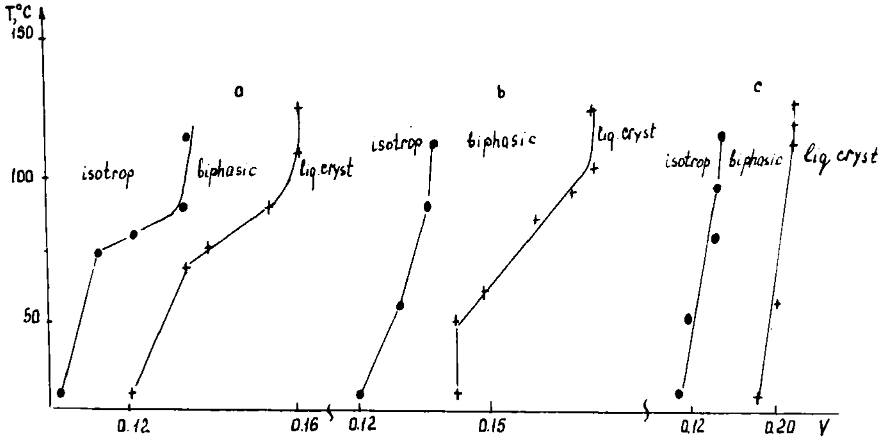

FIGURE 7 The dependence of the boundaries V_2 and V_2' on temperature on the diagrams for the PBG—DMF system a) mol.w. of PBG is 300000; b) mol.w. of PBG is 200000; c) mol.w. of PBG is 120000.

the dissociation of aggregates of macromolecules even near the boiling temperature of the solvent. This is also true for the PBG—DO systems in which the values of V_2 and V_2' are independent of temperature. It should be suggested that the dependencies of the boundaries of the biphasic regions on temperature in PCBL—DMF[7] and poly-*p*-benzamide-sulfuric acid[8] are probably due to the aggregation of the polymers in the systems being investigated. The absence of the dependence of the true boundaries of the biphasic range on temperature shows that the values of the χ parameter approach zero for the PBG—DMF system in the range from 0 to 140°. The true dependence of V_2 for the biphasic region on temperature for the PBG—DMF (mol.w. of polymer = 300000) is shown in Figure 7. Thus, the dependence of the concentra-

TABLE V

Experimental and theoretical values of the parameter of disorientation sin ψ and the parameter of orientation f of the PBG molecules of different asymmetry P

P	Theoretical results data[3]	 data[17]	P	Experimental results	
20	0.167	0.202	23	0.182	0.95 (0.947)†
30	0.172	0.213	32	0.182	0.95
50	0.177	0.218	63	0.216	0.93
			86	0.163	0.96
100	0.186	0.225	111	0.182	0.95
			133	0.230	0.92
∞	0.186	0.232			

† is the theoretical value of f according to Ref 17.

tion boundaries of the coexisting phase on both the geometric asymmetry and the temperature demonstrates good qualitative and quantitative agreement with the lattice model of the formation of the liquid crystalline state.[3]

Finally, let us consider the question of the degree of orientation of the macromolecules in the liquid crystalline domain. The orientational characteristics of the liquid crystalline states in solutions are usually determined when some orientational effect exists. It was shown that in some liquid crystalline systems based on PBG strong homeotropic orientation of the polymers is observed on supports such as KBr, NaCl, and CaF_2.[20] This permits the determination of the orientational parameters of the PBG molecules as a function of their geometric asymmetry by polarized IR radiation. This procedure was used to determine the value of the degree of orientation f from Eq. (3)

$$\left(\frac{D_{\mathrm{AmI}}}{D_{\mathrm{AmII}}}\right)_{\mathrm{or}} \times \frac{1.5\sin^2\theta_{\mathrm{AmII}} + C}{1.5\sin^2\theta_{\mathrm{AmI}} + C} = \left(\frac{D_{\mathrm{AmI}}}{D_{\mathrm{AmII}}}\right)_{\mathrm{non}} \tag{3}$$

where $C = (1 - f)/f$; $(D_{\mathrm{AmI}}/D_{\mathrm{AmII}})_{\mathrm{or}}$ is the ratio of the optical densities observed for the AmideI and AmideII bands in the spectrum of a sample with homeotropic orientation; $(D_{\mathrm{AmI}}/D_{\mathrm{AmII}})_{\mathrm{non}}$ is the same ratio, but without orientation; θ is the angle between the molecular axis and the direction of the transition dipole moment ($\theta_{\mathrm{AmI}} = 34°$, $\theta_{\mathrm{AmII}} = 69.5°$).

According to the lattice model, the theoretical value of the parameter of disorientation was determined as sin ψ, where ψ is the azimuthal angle between the axis of the rod-like particle and that of the preferred orientation. The experimental and theoretical data obtained in 1956 and 1979 on orientation of macromolecules of different mol.w. are shown in Table V. It is clear that the theoretical and experimental results are in good qualitative agreement.

Hence, the behavior of anisotropic polymer particles in concentrated solutions and the formation of the liquid crystalline state are adequately described by the lattice model of Flory. The method of preparation of non-aggregated solutions suggested in this work makes it possible to consider experimentally other problems relating to the formation of the liquid crystalline state predicted by the lattice theory, in particular, the formation of the liquid crystalline state in systems involving various rigidities.[21,22]

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