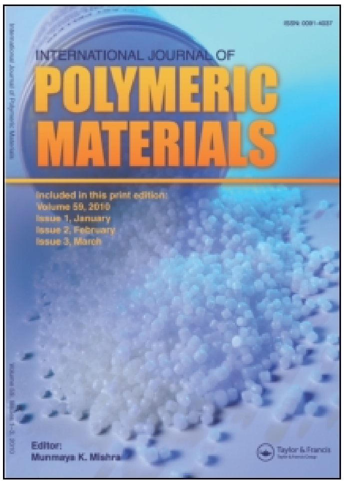
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Rheological Properties of Liquid-crystalline Polymer Solutions

V. G. Kulichikhin[a]; G. I. Kudryavtsev[a]; S. P. Papkov[a]
[a] USSR Research and Designing Institute of Man-Made Fibers, Moskovskaya oblast, USSR

To cite this Article Kulichikhin, V. G. , Kudryavtsev, G. I. and Papkov, S. P.(1982) 'Rheological Properties of Liquid-crystalline Polymer Solutions', International Journal of Polymeric Materials, 9: 3, 239 — 256
To link to this Article: DOI: 10.1080/00914038208077983
URL: http://dx.doi.org/10.1080/00914038208077983

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1982, Vol. 9, pp. 239–256
0091-4037/82/0903-0239 $06.50/0

Printed in Great Britain

Rheological Properties of Liquid-crystalline Polymer Solutions†

V. G. KULICHIKHIN, G. I. KUDRYAVTSEV and S. P. PAPKOV
USSR Research and Designing Institute of Man-Made Fibers, Mytishchi, Moskovskaya oblast, 141009, USSR

(*Received January 14, 1982*)

An analysis is presented of the principal rheological factors inherent in the flow of nematic solutions of rigid-chain aromatic poly(para-amides), viz., viscosity anisotropy, yield points, and viscosity peaks in the region of phase transition on the temperature and the concentration scale, thereby making it possible to use the rheological characteristics to plot phase diagrams.

INTRODUCTION

Studies concerned with the class of rigid-chain polymers revealed new aspects in the field of rheology generally designated as structural rheology. The main characteristic displayed by the solutions of rigid-chain polymers resides in their ability to self-ordering when a specific combination of thermodynamic parameters is operative.[1,2] The anisotropic or liquid-crystalline state of spin dopes is a major prerequisite for the production of high-strength fibers,[2,3] and the basic molecular orientation occurs in this case as early as during spin dope flow through spinneret holes. Hence, in such systems the process of flow, in terms of the preparation of a highly oriented material, is more essential than the conventional techniques of plastification or orientational drawing. This situation emphasizes the theoretical and practical importance of studying the rheological properties of liquid-crystalline solutions of rigid-chain polymers.

Apart from recently published monographs,[2,4] collections of papers[5,6] and review articles[7–9] devoted to the general problems of liquid-crystalline state of polymers, there have appeared papers of a purely rheological nature in which, however, the treatment of the subject is, for the most part, confined to the

---

† Presented at the Symposium on Polymer Rheology held in Suzdal, September 12–16, 1980 (the USSR).

methodological and interpretative aspects of the classical rheology of polymers. An exception to this rule is to some extent provided by the investigations of Ciferri and co-workers[5,14] who attempted to elucidate anomalies in the viscous properties of isotropic solutions of aromatic polyamidhydrazide X-500 in terms of isotropic solution transition, on being strained, into the anisotropic state. Mention may also be made in this connection of the rheoptic studies by Onogi, White *et al.*[15] which underline the importance of accounting for the boundary (wall) layer effect and point to the fact that rheological characteristics are likely to vary in case the experiments on liquid-crystalline solutions of polymers are carried out in rheometers of different geometry. Also of interest is Kawai's paper[16] in which the early experimental data of the present authors[13] on the dependence of the viscosity of poly-p-benzamide (PBA) solutions on the concentration (C) and the molecular mass (M) are interpreted in the light of the decreased degree of liquid-crystalline domain anisometry as compared to the respective characteristic displayed by a rigid-chain macromolecule proper.

As can be seen from the foregoing, the majority of reported investigations employ a conventional rheological approach relying on the measurement of tangential and normal stresses at various shear rates under steady-state and dynamic conditions and involving the calculations of viscosity, the initial factor of normal stresses, dynamic moduli, and other derived characteristics. Practically no attempt, however, has been made to elucidate the specific rheological properties of anisotropic polymer solutions from the standpoint of the physics of liquid crystals, although in this branch of physical science extensive use is made of the concept of viscosity anisotropy[17,18] which is likely to play a key role in clarifying various rheological peculiarities of polymeric lyotropic liquid crystals.

Three principal viscosity coefficients are known which differ from one another in the relative position of long molecular axes and the directions of motion and velocity gradient. As can be seen in Figure 1 adopted from,[19] an appropriate internal-friction coefficient corresponds to a definite orientation of molecules.

In the case of low-molecular liquid crystals, the measurement of various

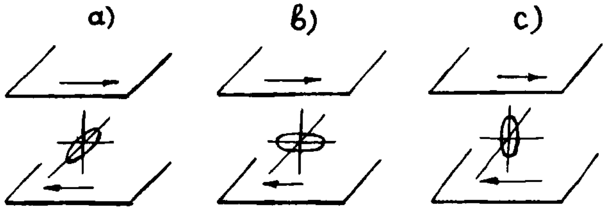


FIGURE 1 Alternative positions of a flowing liquid crystal molecule.

viscosity coefficients is generally performed in a magnetic field that provides for a definite orientation of molecules relative to the direction of flow. This technique was employed for determining the anisotropic viscosity coefficients of nematic methoxybenzylidenebutylaniline which were found to be as follows:[20] $\eta_a = 41.6 \cdot 10^{-3}$; $\eta_b = 23.8 \cdot 10^{-3}$, and $\eta_c = 103.5 \cdot 10^{-3}$ Pa·s (the subscripts *a*, *b* and *c* correspond to different molecular orientations presented in Figure 1).

In the viscometry of polymers, it is general practice to use rotational or capillary viscometers which measure the viscosity close to η_b, but heretofore in the available literature no studies have been reported on the simultaneous determination of rheological parameters and the degree of polymer orientation. The arrangement of a liquid crystal molecule in the gap between the measuring surfaces (the Couette flow) is shown schematically in Figure 2. In the simplest case, the spatial orientation of a molecule can be defined by measuring two angles, viz., ϕ—the mean disorientation angle, and θ—the angle of inclination of the plane accommodating the moving molecules relative to the velocity gradient (the angle θ appears due to the tendency of a stiff molecule to turn in the direction of velocity gradient growth.[17] In the present paper we suggest unsophisticated experimental techniques of assessing the anisotropic viscosity coefficients of liquid-crystalline polymer solutions in the absence of a magnetic field and attempt to correlate the observed effect with the principal rheological characteristics of the systems in question.

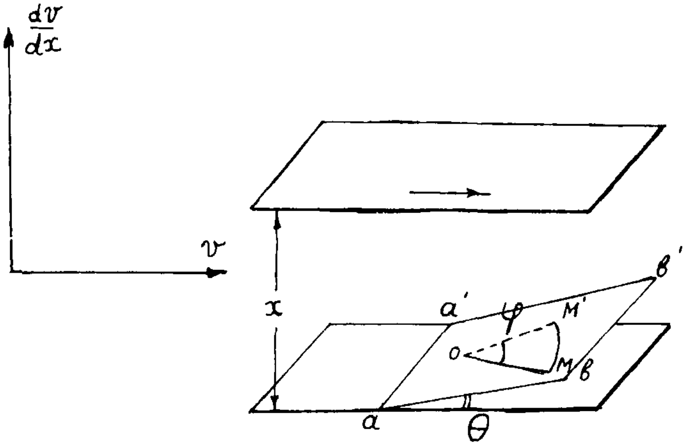


FIGURE 2 Schematic representation of liquid crystal molecule (OM) flow: *aa'bb*—the plane in which molecules are located; θ—the angle of plane inclination relative to the velocity vector; ϕ—the mean disorientation angle within the plane of flow; dv/dx—the velocity gradient in the gap (gap width, x).

EXPERIMENTAL

Methods

To estimate the angle θ, use was made of a flow-through cell comprising two IR radiation-transparent plates, wherein one plate is capable of being displaced relative to the other one at a desired velocity, provided the gap remains constant. The cell was adapted for taking the IR spectra at different angles of plate inclination relative to the optical axis of the spectrophotometer. For the system under consideration, i.e. anisotropic PBA solutions in dimethylacetamide (DMAA) in the presence of 3% LiCl, IR radiation absorption by the solvent in the wavenumber range of from 800 to 1000 cm^{-1} is negligible, thereby making it possible to observe three distinct bands at 805, 860 and 905 cm^{-1} in the polymer spectrum.[21] The 805 cm^{-1} band displays π-polarization, so that as a result of tilting the cell at various angles one might expect the dichroic ratio maximum for this band ($R_{805} = D_{\parallel}/D_{\perp}$) to be obtained at a definite angle of tilt which will be equal to θ.

Presented in Figure 3 is the dependence of R_{805} on the angle of cell tilt in relation to the instrument optical axis. As can be seen from these data, the angle θ corresponding to the maximum of dichlorism, in case the anisotropic 11% solution of PBA flows at a shear rate of 1.5 s^{-1}, is as small as 2 to 3 deg., this angle of tilt being significantly below the theoretically predicted value[23] for isotropic flow of rodlike molecules. This discrepancy is in no way surprising since the angle of tilt generally reported to be 45 deg. (for low shear rates) depends on the rotational Brownian motion of anisodiametric particles which for liquid-crystalline solutions plays no decisive role because here the

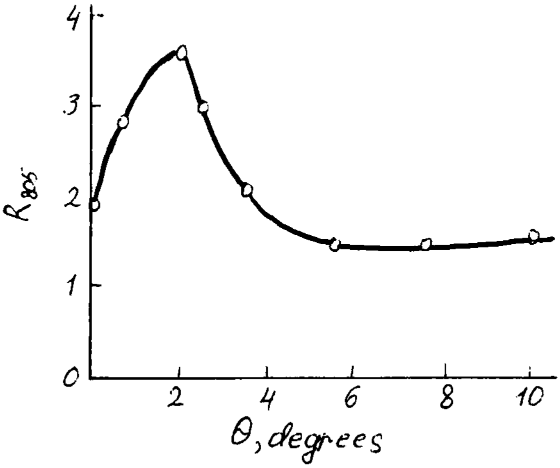


FIGURE 3 Dependence of dichroic ratio R_{805} on the angle θ.

macromolecules are divested of their individuality and there occurs the flow of concerted aggregates (domains). However, the angle θ for PBA solutions is also much smaller than that found for low-molecular liquid crystals (10–15 deg.)[17] and this situation provides grounds for assuming in subsequent experiments that polymer molecules, when in the state of flow, are disposed practically completely in the shear plane, so that, in order to define the orientation, it would be sufficient to determine only the angle ϕ using the above-identified dichroic ratio for the 805 cm^{-1} π-band.[22]

The viscosity coefficients corresponding approximately to the cases (a) and (b) in Figure 1 were tentatively evaluated in a coaxial cylinder assembly of the rotational viscometer "Rheotest" (DDR) modified as follows:[24] the fixed outer cylinder was replaced for a new one having a glass cylindrical part, the gap width (2.0 ± 0.2 mm) remaining unchanged. The torque applied to the inner cylinder, which is a measure of the "longitudinal" viscosity $\eta_{\parallel}$ (this parameter is close to η_a, but is not equal to it because no ideal orientation of the test specimen in the direction of flow is attainable), was determined simultaneously with measuring the falling time of a ball 0.37 mm in dia. in the gap between the cylinders, followed by calculating the "transverse" viscosity $\eta_{\perp}$ (this parameter approximates to the value of η_a, but is not equal to it) according to the Stokes formula corrected for the wall effect in the measuring cell. Earlier the layout described above was effectively employed[25] for studying the sedimentation of disperse phase particles from flowing polymer suspension.

The velocity $\dot{\gamma}_{\parallel}$ attained in the course of determining the viscosity coefficient η_b was assumed to be a measure of the strain rate. The overall strain due to complex shear was disregarded because velocity gradient variation during the falling time of the ball was minute (on the average, a 1.5-fold variation), while the value of $\dot{\gamma}_{\parallel}$ charged significantly (from 10^{-1} to 10^{2} s^{-1}). At least 10 measurements were made as a rule for each $\dot{\gamma}_{\parallel}$, 80% of the measurement results being in good agreement. In 20% of the experiments, in which the ball missed the gap center and was displaced under the action of the centrifugal force onto the wall, the falling time of the ball exceeded by a factor of 1.5 to 2.0 the mean falling time at a given velocity. This phenomenon is presumably associated with the existence of an extended boundary (wall) layer, the thickness of which was earlier estimated to be 0.015 mm.[21] Accordingly, in the final analysis such measurements were discarded.

As can be seen from the description of the experimental layout used, the orienting effect of a magnetic field was not resorted to primarily due to the fact that orienting the viscous anisotropic solution PNA in a magnetic field is fairly long process, the intermediate stages of which involve the formation of domain structures, wherein molecular orientation variations within a domain obey a sophisticated law.[21,26] Although, by way of comparison with the techniques relaying on the forced orientation of test specimens, the suggested method is less unambiguous as regards correlating the viscosity coefficients being measured to η_a and η_b, it nonetheless is capable of revealing the differences between $\eta_{\parallel}$ and $\eta_{\perp}$, i.e. of demonstrating the existence of viscosity anisotropy.

Viscosity measurements, as noted above, were paralleled by the evaluation of the average angle of disorientation, ϕ, using the through-flow cell mounted on a spectrophotometer.

To evaluate the viscosity coefficient η_c corresponding to the flow of a nematic liquid crystal with the long molecular axes disposed at right angles to the direction of shear and parallel to the velocity gradient in the absence of an orienting effect due to a magnetic field, a unique instrument was developed comprising two vessels interconnected by a calibrated tube and an air duct.[24] The calibrated tube made in the form of a flat capillary serves for attaining the homeotropic texture of a nematic phase which is a thermodynamically preferred texture of anisotropic solutions of PBA. Solution flow in this viscometer occurs due to the difference between the levels in the communicating vessels obtained by tilting the microscope stage and by turning the flat cells on the stage. In this experiment, the shear stress is calculated from pressure drop, while the strain rate is assessed using the linear shift velocity of a reference, a suitable reference being, for example, disinclination.

RESULTS AND DISCUSSION

Viscosity anisotropy

The dependence of $\eta_{\parallel}$, $\eta_{\perp}$, and ϕ values on $\dot{\gamma}_{\parallel}$ is presented in Figure 4. Increasing the strain rate results in "longitudinal" viscosity diminution and "transverse" viscosity growth, while at $\dot{\gamma}_{\parallel} \geqslant 10\ \mathrm{s}^{-1}$ the rate of change of the viscosity components drops as the strain rate grows, so that the $\eta_{\parallel}$ and $\eta_{\perp}$ values being measured may be assumed at $\dot{\gamma}_{\parallel} > 10\ \mathrm{s}^{-1}$ to asymptotically approach a limiting value. The limiting values of $\eta_{\parallel}$ and $\eta_{\perp}$ recorded experimentally have been found to be 0.7 and 1.2 Pa$\cdot$s, respectively. In this case of equiviscous isotropic solutions, the "longitudinal" and the "transverse" viscosity component are one and the same within the experimental error limit.

Luminescence (texture bend) in the absence of visible flow (region I in Figure 5) appears initially in the field of vision of a polarizing microscope (with the polaroids crossed) as a result of straining the homeotropic specimen. Once the shear stress of about $4.0 \cdot 10^{-2}$ Pa has been attained, there sets on a slow flow at a linear velocity of $\sim 10^{-4}$ mm/s which corresponds to the viscosity of ~ 2.5 Pa$\cdot$s (the extreme left-hand point in region II). Gradually releasing the stress (cf. the histogram) results at an early stage not in increasing, but in decreasing the viscosity. Viscosity growth commences again only at $\tau = 1.5 \cdot 10^{-2}$ Pa and is accompanied by the recovery of the undistorted homeotropic texture of the solution.

The experiments of this type make it possible to establish the existence of a yield point (τ_y) in polymeric liquid crystals and the onset of thixotropic effects at stresses above τ_y. As regards the absolute value of the viscosity coefficient η_c,

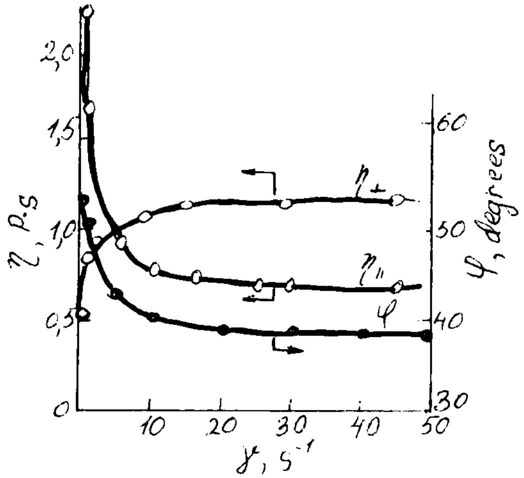


FIGURE 4 Dependence of viscosity coefficients $\eta_{\parallel}$, $\eta_{\perp}$ and the mean disorientation angle ϕ on shear rate.

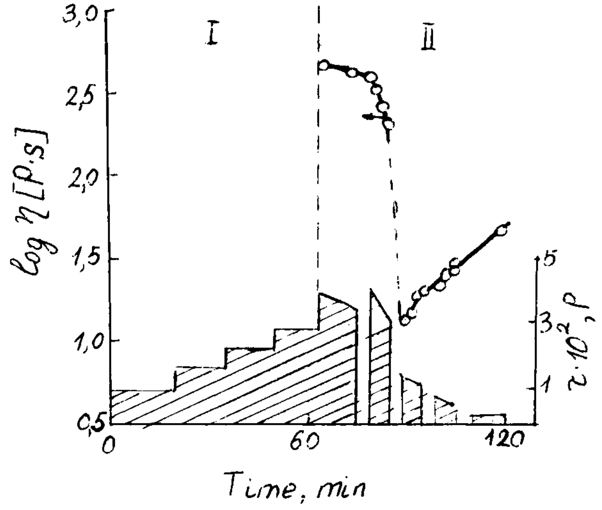


FIGURE 5 Time dependence of viscosity at different shear stresses (indicated on the histogram) for PBA solution having initially a homeotropic texture. No flow in region I; flow occurs in region II.

the value of $\simeq 2.5$ Pa • s will be obtained by assuming arbitrarily that the first point plotted on transition from region I to region II corresponds to the sought-for magnitude. The feasibility of planar layer formation is not excluded as the value of τ increases further in which case a mixture would be involved in the flow. In view of the assumptions referred to above, the following values appear to be reasonable: $\eta_{\perp}(\eta_a) = 1.2$ Pa • s; $\eta_{\parallel}(\eta_b) = 0.7$ Pa • s, and $\eta_c \geqslant 2.5$ Pa • s. Hence, the tendency inherent in the variation of these values remains the same as in the case of low-molecular liquid crystals.

As pointed out earlier, the investigations reported here are concerned with providing evidence to demonstrate the existence of the effect of viscosity anisotropy in polymer systems rather than with establishing precise values of anisotropic viscosity coefficients. This approach is dictated by the fact that the effect of viscosity anisotropy is so potent that it exerts influence on the fundamental rheological characteristics of polymeric nematics. The manifestations of this effect are systematically discussed below.

Flow curves of anisotropic solutions

It follows from the graph of Figure 4 that the variation of the average disorientation angle ϕ parallels that of the viscosity $\eta_{\parallel}$, this observation being indicative of the relationship between the viscosity measured by the conventional techniques and after-orientation of macromolecules along the direction of flow. The property in question appears to be common for all liquid crystals as evidenced, for example, by Porter and Johnson review[27] devoted to low-molecular thermotropic liquid crystals. The flow curve of nematic p-azoxyanisole at various temperatures presented in Figure 6 shows this compound in the region of liquid-crystalline state to display anomalous viscosity at low shear rates, whereas the isotropic melts of this compound are Newtonian fluids in the entire range of $\dot{\gamma}$ values.

The situation is by far more intricate in the case of polymer systems, since here isotropic solutions and melts are noted for their high degree of structurization. From the rheological standpoint, the structure of isotropic polymer systems comprises a fluctuating network of intermolecular contacts, the disintegration of which due to strain onset is responsible for viscosity anomaly.[28] Once the critical concentration of transition into the liquid-crystalline state (C^x) has been atained, there occurs fluctuating network rearrangement into a system of nematic domains, wherein the orientation of macromolecules is perfect and the thermodynamic considerations (the minimum of free energy) underlie the stability of this orientation. In the interval between the concentrations C^x and C^{xx}, two phases, viz., the isotropic and the anisotropic phase, coexist or, in other words, two interaction types are operative (the fluctuating network and dispersive attraction-repulsion), while

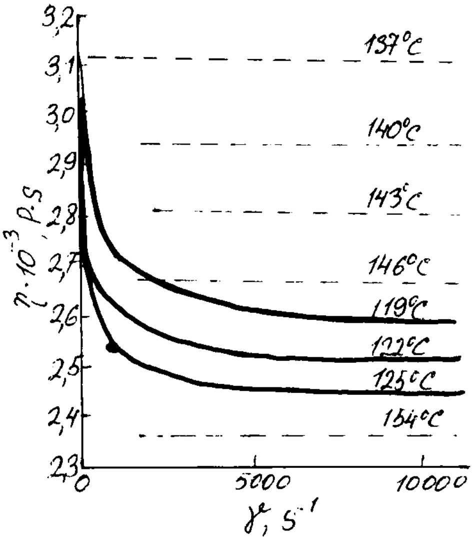


FIGURE 6 Shear rate dependence of p-azoxyanisole viscosity at various temperatures indicated on the graph.

above C^{xx} the anisotropic phase alone is present.[1] It would be of interest to trace how the evolution of structure and interaction pattern would affect the shape and position of flow curves.

The shear stress dependence of viscosity at different concentrations of PBA solutions in DMAA containing 3% LiCl is illustrated in Figure 7.[13] For the PBA specimen studied, the critical concentration of transition to the liquid-crystalline state (C^{x}) equals about 5% at room temperature. The concentration at which this transition is complete (C^{xx}), as evidenced by the formation of a single-phase liquid crystal, equals 8%.

In relatively dilute solutions ($C < C^{x}$), a clear-cut region of Newtonian flow is observed at low shear stresses, and a region of structural viscosity appears at greater stresses. The pattern of rheological behavior of more concentrated solutions ($C > C^{x}$) is fundamentally different. Here a region is also present, in which viscosity diminution is relatively slight and which may be regarded as a quasi-Newtonian flow region, but as τ continues to decrease, the viscosity begins to grow. This region lends itself to facile interpretation in the light of the effects discussed above. In particular at low shear stresses there exists the yield point τ_y (the strength of a liquid-crystal matrix in terms of matrix fragmentation into flow elements) with the adjoining branch of orientational viscosity decrease analogous to that shown in Figure 4.

Increasing the solution concentration results in viscosity drop and yield point growth, while the degree of viscosity anomaly decreases at $\tau \gg \tau_y$.

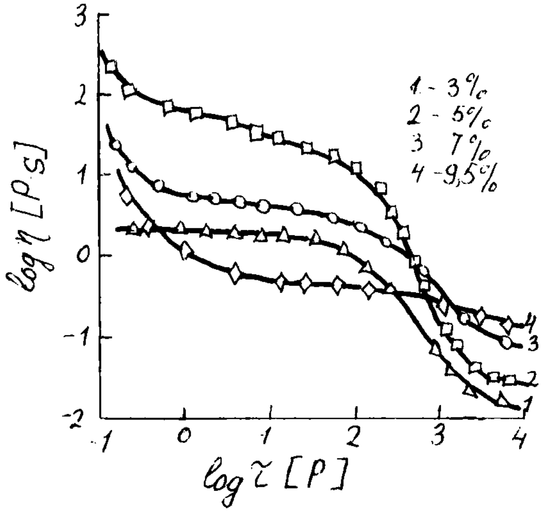


FIGURE 7 Flow curves of PBA solutions at concentrations of 3(1), 5(2), 7(3), and 9.5%(4) at 20°.

Moreover, if the region of stresses adjoining the yield point is excluded from consideration, then the anisotropic solutions display a less pronounced viscosity anomaly than do the isotropic solutions. As emphasized earlier, this is a manifestation of the fundamental dissimilarity in the rheological behavior of polymeric and low-molecular liquid crystals. In the first case, the isotropic system itself exhibits a complex of nonlinear effects (viscosity anomaly, elastic and thixotropic properties), while in the second instance the isotropic melts of low-molecular liquid crystals are the Newtonian fluids. At concentrations in the range of from C^x to C^{xx}, the main contribution to the viscosity anomaly in the anisotropic solutions of rigid-chain polymers would, therefore, be provided by the fragmentation of the fluctuating entanglement network, while at $C > C^{xx}$ the anisotropic solutions might be more Newtonian than are the isotropic solutions.

Hence, a not infrequent contention that liquid crystals display a higher degree of viscosity anomaly than do isotropic melts (solutions) is fully valid for low-molecular systems only, whereas as regards the polymeric nematics its validity is confined to region of stresses adjoining the yield point and the branch of orientational viscosity decrease.

The problem of the elementary unit of liquid-crystalline material flow remains obscure. It is feasible, and the present authors share this viewpoint, that the flow in question involves aggregates (domains), in which case three regions corresponding to different plastic deformation mechanisms can be discerned on flow curves. In region I (cf. Figure 1) the solution, on having passed over the yield point τ_y, behaves like a viscoplastic body and in domain orientation there occurs practically no change. In the region of transition from I to II (embodiment of the situation b) in Figure 1 at the domain level), the orientational processes become prominent. In region II, the flow involves aggregates having an approximately one and the same size and the orientation degree (the values of viscosity for plotting viscosity versus concentration and temperature curves are taken on this branch). In region III, the size and orientation of flow aggregates can vary as a result of liquid crystal fragmentation and flux eddying.

Dependence on solution concentration on rigid-chain polymer concentration

The general pattern of the concentration dependence of "quasi-Newtonian" viscosity (η_q) for the PBA solutions in DMAA containing 3% LiCl is presented in Figure 8 (curve I). Here the viscosity maximum corresponds to the inversion point of the iso- and anisotropic phases. The descending branch of the plot $\eta_q = f(C)$ is associated with the aforementioned change in the mechanism of solution flow.

Specifically, viscosity anisotropy is the principal cause of viscosity diminution when the solution concentration exceeds C^x. Indeed, while in a flowing isotropic solution the existence of the (a), (b), and (c) orientations is equiprobable (Figure 1), the anisotropic solution is characterized by the prevalence of the "least viscous" orientation (b) as a result of the ability of liquid-crystalline aggregates to undergo orientation.

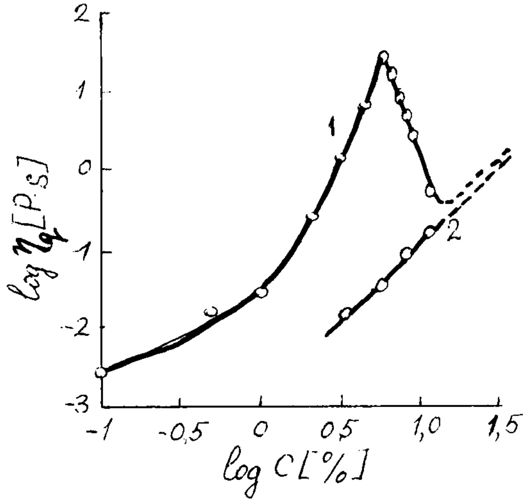


FIGURE 8 Concentration dependence of PBA solution viscosity on a logarithmic scale. Curve 1—viscosities at a shear stress of 10 Pa; Curve 2 – viscosities at a shear stress of 4.000 Pa.

These observations pertain to the region of moderate shear stresses, in which there sets on quasi-Newtonian flow. At high shear stresses, the viscosity versus concentration curve is devoid of a characteristic maximum at C^x, but viscosity grows monotonously with increasing concentration in the same way as in the case of isotropic solutions (curve 2 in Figure 8). This phenomenon can be ascribed to the disintegration of anisotropic structures, as evidenced by field of vision darkening when the solution of interest is examined in a polarizing microscope flow-through cell at high values of $\dot{\gamma}$. An analogous effect was found earlier[10] to occur in the anisotropic solutions of polypeptides, although here system amorphization is likely to be caused by the helix-to-coil transition.

Curve 2 appears to be the limiting case of concentration dependence and quasi-Newtonian viscosity (at $C > C^{xx}$), provided no phase transition would occur at high values of C. The constancy of η_q at $C \gg C^{xx}$[10] or even η_q diminution[29] observed occasionally should, therefore, be regarded not as general regularities, but rather as specific cases. In principle, viscosity η_q variation at $C > C^{xx}$ should follow the broken line in Figure 8. If, however, under these conditions there occurs solution crystallization observed[31] for PBA and poly-p-phenyleneterephthalamide (PPTA) solutions in sulfuric acid, viscosity at high concentrations grows much more abruptly (Figure 9).

The effect of molecular mass on the concentration dependence of viscosity is illustrated in Figure 10. With increasing M, the C^x values are shifted towards

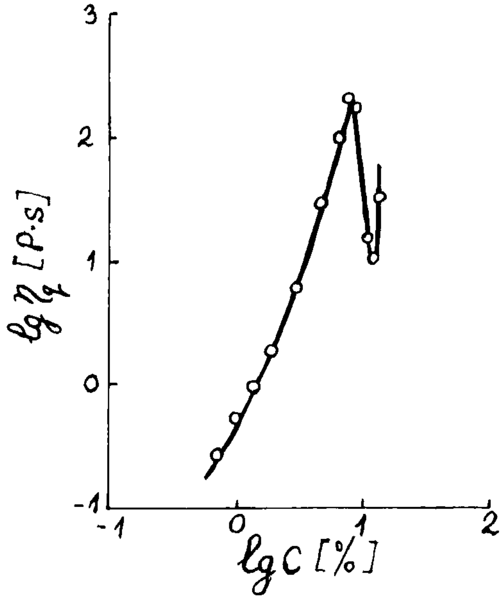


FIGURE 9 Concentration dependence of viscosity of PBA solutions in sulfuric acid at 20°.

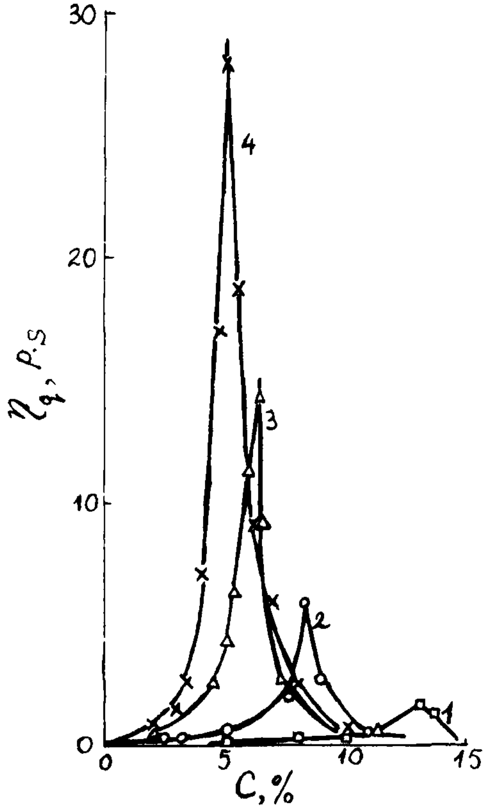


FIGURE 10 Concentration dependences of viscosity of PBA solutions in DMAA. Molecular masses: $11\cdot10^3(1)$; $17.5\cdot10^3(2)$; $22.2\cdot10^3(3)$; and $29.2\cdot10^3(4)$.

lower concentrations, while the maximum absolute value of viscosity, $\eta_{\max}$, and the slope of viscosity *vs.* concentration curves increase. The maximum viscosity value seems to be a quite definite physical characteristic of the material, this assumption being based on the fact that the values of $\eta_{\max}$ and M are interrelated by the power law, viz., $\eta_{\max} = 1.82\cdot10^{-12}\ M^{3.2}$ (for PBA solution), and the exponent is close to the universal value (3.4). The PBA solutions of different molecular masses at the phase transition point (or equidistant therefrom) may, therefore, be considered as being in corresponding or equivalent states. When concentration equality is taken as a basis of comparison (like in the case of the solutions of flexible-chain polymers), then the exponent for the isotropic solutions of rigid-chain polymers may be as high as about 8 (for PBA)[13] or 6.8 (for PPTA).[30]

The concept of rheological state equivalence in the solutions of rigid-chain polymers, which are equidistant from C^x, is substantiated by plotting the

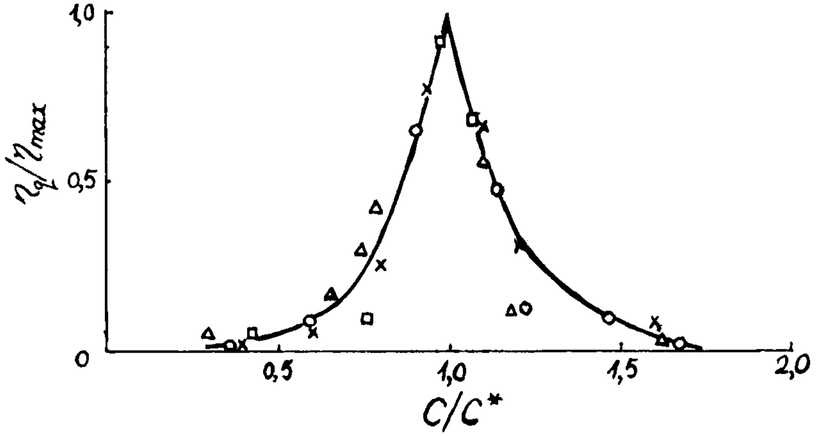


FIGURE 11 Generalized dependence of viscosity of PBA solutions in DMAA on concentration (for notations, cf. Figure 10).

individual functions $\eta_q = f(C)$ in $\eta/\eta_{\max} - C/C^x$ coordinates (Figure 11). The viscous properties of these solutions are, therefore, governed by their distance from C^x.

To sum up the discussion of this aspect of the problem, it should be emphasized that the concentration dependence of viscosity makes it possible to determine with adequate accuracy the value of C^x, i.e. the point of phase transition at constant temperature. However, any point on the phase diagram of a polymer-solvent system is defined by a particular combination of concentration and temperature. Accordingly, the subsequent treatment of the problem will be devoted to temperature-dependent variation in the viscosity of rigid-chain polymer solutions.

Temperature dependence of the viscosity of rigid-chain polymer solutions

Figure 12 illustrates the temperature dependence of viscosity of PBA solutions in sulfuric acid which undergo transition to the liquid-crystalline state at concentrations higher than 8–9%. At lower concentrations, the examined systems experience no changes whatsoever in the temperature range of from 20 to 100° (the relationships $\ln \eta = f(1/T)$ are linear). Anomalous behavior commences at a concentration of 9% and manifests itself in the existence of a viscosity maximum at definite temperatures. The temperature that corresponds to the viscosity maximum will be denoted as T^x (above this temperature, the solution is totally isotropic), while T^{xx} stands for the temperature, at which there commences viscosity growth (isotropic phase appearance). Highly concentrated solutions ($C > 13\%$) experience hardening

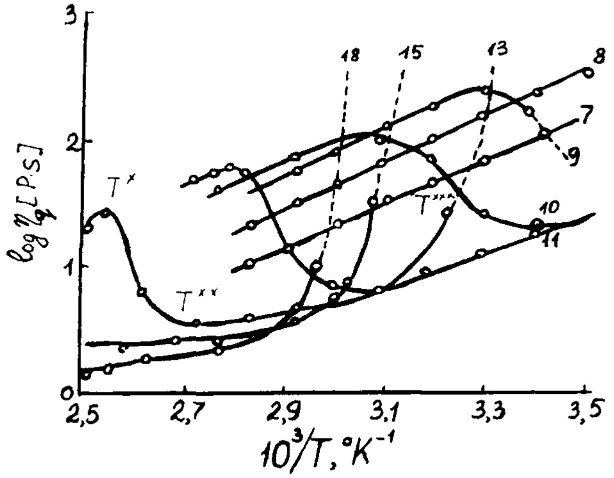


FIGURE 12 Temperature dependence of viscosity for PBA solutions of various concentration in sulfuric acid. Concentrations are indicated on curves.

at low temperatures due crystallosolvate phase emergence[31] therein. When heated to the temperature T^{xxx}, the solutions acquire the liquid-crystalline state.

Viscosity variations at T^{x} and T^{xx} transitions can be readily interpreted in terms of the effects discussed hereinabove. Isotropic phase accumulation results in increasing the share of a statistical mixture of macromolecules having (a), (b) and (c) orientations and interconnected with one another by the fluctuating entanglement network, whereby the viscosity is caused to grow. A major portion of the temperature range between T^{xxx} and T^{xx} is characterized by a practically unitary temperature dependence of viscosity in the solutions of different concentrations. In the present context, the term "unitary" is meant to denote not only the constancy of flow activation energy (*ca.* 23 kJ/mol), but also one and the same value of the preexponential factor in the Arrhenius equation. This finding points to the constancy of the kinetic flow unit under these conditions and, therefore, is indirectly indicative of the presence of aggregate flow having the (b) orientation.

At $T > T^{x}$, the temperature dependence of viscosity likewise obeys an exponential equation (the flow activation energy varies but little with concentration and is close to 35–38 kJ/mol).

The generalized temperature and concentration dependence of viscosity is given in Figure 13, which clearly shows the following features; the direction of the "ridge" corresponding to the viscosity maximum and, hence, to the transition from the isotropic to the anisotropic state; the region of viscosity growth resulting in complete flowability loss in the solutions; and the

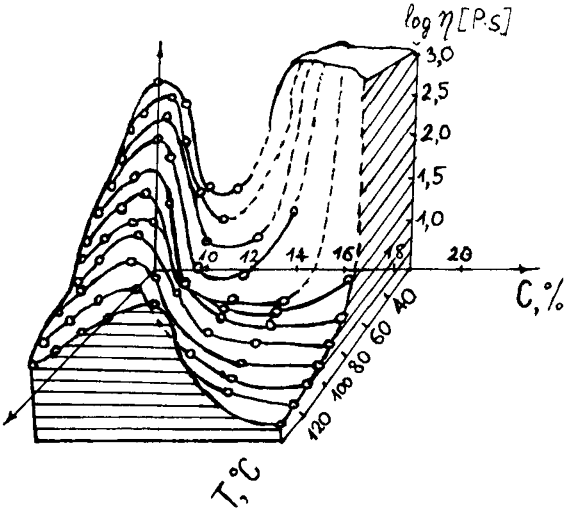


FIGURE 13 Effect of temperature and concentration on the viscosity of PBA solutions in sulfuric acid (molecular mass, 10^4).

"plateau", which provides maximum convenience for processing these solutions, inasmuch as the undisputably liquid-crystalline solutions possess on the "plateau" the lowest viscosity. The aforementioned relationships provide the possibility of directly evaluating the position of phase boundaries in rigid-chain polymer solutions.

Thus, viscometric data alone are adequate for ascertaining the position of the narrow biphasic region on the diagram of state (Figure 14). The trend of the $T^{xxx}(C^{xxx})$ can likewise be determined by a rheological technique, namely, by the penetrrometric method. Moreover, phase boundaries were delineated by the polarization-optical and thermographic methods, the transition points obtained by different methods being coincident within the experimental error limit. Without going into the details of the phase diagram for the PBA-H_2SO_4 system (special studies, e.g. Ref. 31, are devoted to this problem), four principal regions should be noted on this diagram: I—isotropic solution; II—a mixture of isotropic and anisotropic phases; III—liquid-crystalline solution, and IV—crystallosolvate.

A further peculiarity in the rheological properties of rigid-chain polymer solutions stems from the above discussion, viz., the feasibility of employing rheological characteristics for plotting the diagrams of state for a polymer-solvent system.

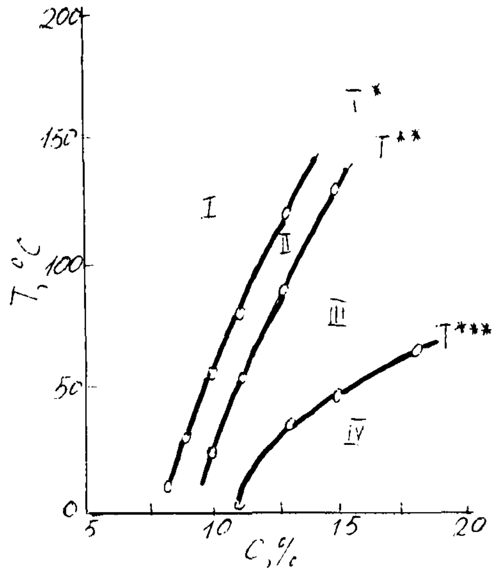


FIGURE 14 Diagram of state for PBA-H_2SO_4 system (see text for explanation).

References

1. P. J. Flory, *Proc. Roy. Soc.* **234A,** 60 (1956).
2. S. P. Papkov and V. G. Kulichikhin, *Liquid-Crystalline State of Polymers* (Khimiya P. H., Moscow, 1977), p. 240 (in Russian).
3. S. L. Kwolek, U.S. Patent No. 3,671,542 (1972).
4. D. K. Eliashevich, V. G. Kulichikhin, S. G. Kulichikhin, V. D. Fikman and S. Ya. Frenkel, *Orientation Phenomena in Polymeric Solutions and Melts* (Khimiya P. H., Moscow, 1980) (in Russian).
5. *Ultra-High Modulus Polymers*, ed. by A. Cifferi and I. M. Ward (Academic Press, London, 1979).
6. *Liquid Crystals and Ordered Fluids, vol. 2*, ed. by R. S. Porter and J. F. Johnson (Academic Press, New York, 1974).
7. S. P. Papkov, *Vysokomolekul. Soedin.* **19A,** 923 (1977).
8. V. P. Shibaev and N. A. Plate, *Vysokomolekul. Soedin.* **19A,** 923 (1977).
9. J. L. White and J. F. Fellers, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **33,** 137 (1978).
10. E. Izuka, *Mol. Cryst. Liq. Cryst.* **25,** 287 (1974).
11. G. Kiss and R. S. Porter, *Polym. Prepr.* **18,** 185 (1977).
12. D. G. Baird, *J. Appl. Polym. Sci.* **22,** 2701 (1978).
13. S. P. Papkov, V. G. Kulichikhin, V. D. Kalmykova and A. Ya. Malkin, *J. Polym. Sci., Polym. Phys. Ed.* **12,** 1753 (1974).
14. G. C. Alfonso, E. Bianchi, A. Gifferi, S. Russo, F. Salaris and B. Valenti, *J. Polym., Sci., Polym. Symp.* No. **65,** 213 (1978).
15. Y. Onogi, J. L. White and J. F. Fellers, *J. Polym. Sci., Polym. Phys. Ed.* **18,** 663 (1980); *J. Non-Newton. Fluid. Mech.* **7,** 121 (1980).
16. T. Kawai, *Makromol. Chem. Rapid. Commun.* **1,** 187 (1980).
17. P. G. de Gennes, *The Physics of Liquid Crystals* (Oxford, 1974) p. 333.
18. E. L. Aero and A. N. Bulygin, *Hydromekhanika* **7,** 106 (1973).

19. P. Pieranski and E. Guyon, *Phys. Rev.* **9A,** 404 (1974).
20. Ch. Gähwiller, *Phys. Lett.* **36A,** 311 (1971).
21. V. A. Platonov, G. D. Litovchenko, T. A. Belousova, L. P. Milkova, M. V. Shablygin, V. G. Kulichikhin and S. P. Papkov, *Vysokomolekul. Soedin.* **17A,** 221 (1975).
22. M. V. Shablygin, T. A. Belousova, V. G. Kulichikhin, V. A. Platonov, V. D. Kalmykova and S. P. Papkov, *Vysokomolekul. Soedin.* **18A,** 942 (1976).
23. V. N. Tsvetkov, *Newer Methods of Polymer Characterization,* ed. by B. Ke (Interscience Publ., 1964) Ch. 14.
24. V. G. Kulichikhin, N. V. Vasil'eva, V. A. Platonov, A. Ya. Malkin, T. A. Belousova, O. A. Khanchich, A. V. Volokhina and S. P. Papkov, *Vysokomolekul. Soedin.* **21A,** 1407 (1979); *Kolloidn. Zh.* **16,** 200 (1979).
25. D. J. Highgate and R. W. Whorlow, *Brit. J. Appl. Phys.* **18,** 1019 (1967).
26. V. A. Platonov, G. D. Litovchenko, V. G. Kulichikhin, M. V. Shablygin, V. D. Kalmykova and S. P. Papkov, *Lhim. Volokna* No. **4,** 36 (1975).
27. R. S. Porter and J. F. Johnson, *Rheology,* ed. by F. Eirich (New York, 1967), p. 317.
28. T. G. Fox, *J. Polym. Sci.* **9C,** 35 (1965).
29. V. G. Kulichkhin, A. Ya. Malkin, S. P. Papkov, O. N. Korol'kova, A. V. Volokhina and O. B. Semyonov, *Vysokomolekul. Soedin.* **16A,** 169 (1964).
30. D. G. Baird and R. L. Ballman, *J. Rheol.* **23,** 505 (1979).
31. S. P. Papkov, *Vysokomolekul. Soedin.* **21B,** 787 (1979).