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## Nematic solutions of nematic side chain polymers : twist viscosity effect in the dilute regime

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**Résumé.** — Nous avons montré que la viscosité de torsion d'un nématique est notablement augmentée par l'addition de chaînes polymériques, même à faible concentration. Cet effet est analysé en fonction de la longueur des chaînes et du paramètre d'ordre. Les résultats expérimentaux sont en bon accord avec un modèle qui implique une conformation anisotrope du polymère ; ils conduisent à une estimation numérique de cette anisotropie, qui semble suffisamment importante pour pouvoir être mesurée directement par une méthode de diffusion aux petits angles.

**Abstract.** — We have shown that the twist viscosity of a nematic medium is largely increased when adding polymeric chains, even in a low concentration regime. This effect is analysed in terms of the chain length and the nematic order parameter. The experimental results are in good agreement with a model implying an anisotropic conformation of the polymeric backbone ; they allow a numerical determination of the anisotropy, which appears large enough to be directly measured by a small angle scattering technique.

### Introduction

In the past five years, there has been a growing interest in mesomorphic polymers. These polymers present a large range of chemical and structural varieties [1]. We were interested in one such system, side chain thermotropic polymers, with the general aim of understanding how the behaviour of the flexible backbone is coupled to the specific liquid crystal properties. One possible approach in this new field consists of studying some physical properties of very dilute solutions of such polymers, in a conventional, low molecular weight, liquid crystal solvent. As for ordinary flexible chains in ordinary isotropic solvents, these procedures allow one to deal with a one-chain problem, that may presumably be simply interpreted. Moreover, one may induce, by analogy with the classical case, that the hydrodynamic properties of such solutions are very sensitive to the presence of small amounts of polymer, because of the large

volume fraction occupied by swollen macromolecules. In a mesomorphic, say nematic medium, the situation appears rather rich and new, due to the very specific features of « nematodynamics » which necessitates several (five) viscosity coefficients to describe the dissipative processes in those anisotropic fluids [2]. In fact, F. Brochard [3] has calculated the effect of dissolved polymers on different viscosity coefficients characteristic of a nematic medium.

In this article, we describe experimental results concerning the twist viscosity coefficient,  $\gamma_1$ , which is totally specific to a nematic liquid, in the way that it characterizes the viscous coupling between the fluid and the nematic director. We discuss the observed effects as a function of concentration, order parameter and molecular weight of the polymers, in the framework of the F. Brochard model. From this comparison, we get quantitative information on the anisotropy of the conformation of the main flexible chain.

### 1. Experimental section.

**1.1 POLYMERS.** — All the compounds used here were synthesized at the Institut für Physikalische Chemie, Clausthal. They are derivatives of poly(methylsiloxane), where mesogenic phenyl benzoate groups are grafted to the main chain *via* flexible methylene spacers, as schematized in figure 1. In this study, we vary two parameters : the degree of polymerization,  $N$ , which defines the total length of the main chain, and the number of methylene groups in the spacer,  $n$ , which determines the strength of the coupling between the backbone and the mesogenic moieties. The formulae and clearing temperatures,  $T_c$ , for the different polymers, denoted by  $P_N^n$ , are given in table I.

**1.2 NEMATIC SOLUTIONS.** — We obviously need to use a low molecular weight (l.m.w.) liquid crystal which is a good solvent in the nematic phase for the  $P_N^n$  polymers. One might *a priori* expect that phenylbenzoate derivatives are good candidates, as they are chemically similar to the mesogenic parts of the polymers. In fact, careful phase diagram studies [4, 5] have shown that this problem is much more compli-

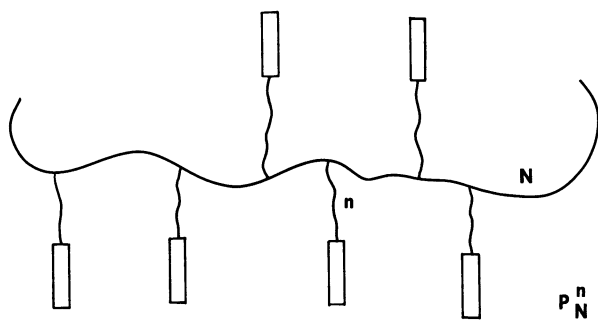


Fig. 1. — Schematized representation of polymers  $P_N^n$ .

cated, and that miscibility gaps may appear, in isotropic and nematic phases, sensitively depending on the length of the end chains in l.m.w. compounds. It has been checked that, for the derivative denoted by M in table I, a total miscibility in the nematic range is obtained for the three  $P_N^n$  polymers we consider ; consequently, we may estimate that M is a « good solvent » and it is used throughout this study. However, due to the presence of an unsaturated link in M, it is necessary to check for chemical degradation, specially when heated ; therefore, we always record the clearing temperature  $T_c$  for the pure compound or mixtures we used before and after the physical experiments, and take into account the eventual shift of  $T_c$  in the data analysis.

To obtain homogeneous mixtures of  $P_N^n$  in M, three days of slow shaking in an heated bath was necessary ; we vary the concentration  $c$  (in weight) in the range 0 to  $4 \times 10^{-2}$  for the different  $P_N^n$ . In the following, we shall use  $\Phi$ , number of chains per unit volume, rather than  $c$ , for characterizing the mixtures ( $0 < \Phi < 10^8$  ch/cm<sup>3</sup>). All the solutions we used are presented in table II.

**1.3 EXPERIMENTAL PROCEDURE.** — As we are trying to show differential effects between pure solvent and dilute solutions, we need high accuracy when measuring the viscosity coefficient  $\gamma_1$ . This is probably best insured by using the analysis of the dynamics of a Fredericks transition, following the method described in details by Pierański *et al.* [6] : starting from an homogeneous sample, uniaxially oriented in the planar geometry between two glass slides, we apply a magnetic field  $H$  perpendicular to the initial director axis ; an angular distortion appears when  $H$  is larger than a critical value  $H_c$  ;  $H_c$  is related to the splay elastic constant,  $K_1$ , the diamagnetic susceptibility anisotropy  $\chi_a$  and the thickness of the sample,  $d$ .

Table I. — Symbols, formulae and clearing temperature  $T_c$  for the pure nematic materials.

Symbol	Formula	$T_c$ (K)
$P_{95}^4$	$\begin{array}{c} \text{CH}_3 \\ (-\text{Si}-\text{O}-)_{95} \\ (\text{CH}_2)_4-\text{O}-\phi-\text{COO}-\phi-\text{OCH}_3 \end{array}$	376
$P_{95}^6$	$\begin{array}{c} \text{CH}_3 \\ (-\text{Si}-\text{O}-)_{95} \\ (\text{CH}_2)_6-\text{O}-\phi-\text{COO}-\phi-\text{OCH}_3 \end{array}$	385
$P_{50}^6$	$\begin{array}{c} \text{CH}_3 \\ (-\text{Si}-\text{O}-)_{50} \\ (\text{CH}_2)_6-\text{O}-\phi-\text{COO}-\phi-\text{OCH}_3 \end{array}$	379
M	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{O}-\phi-\text{COO}-\phi-\text{OC}_6\text{H}_{13}$	360

Table II. — Values of polymer concentrations and clearing temperatures for the nematic mixtures.

Mixture	$c$ (g/g)	$\Phi$ (ch/cm <sup>3</sup> )	$T_c$ (K)
M + P <sub>95</sub> <sup>4</sup>	0.90 %	$1.6 \times 10^{17}$	359.3
	1.80 %	$3.2 \times 10^{17}$	359.4
	2.37 %	$4.2 \times 10^{17}$	362.2
	3.91 %	$6.9 \times 10^{17}$	362.6
M + P <sub>95</sub> <sup>6</sup>	0.95 %	$1.5 \times 10^{17}$	359.9
	2.53 %	$4.1 \times 10^{17}$	361.6
	3.3 %	$5.4 \times 10^{17}$	362.8
M + P <sub>50</sub> <sup>6</sup>	1.04 %	$3.2 \times 10^{17}$	361.8
	1.98 %	$6.1 \times 10^{17}$	362.2

$$H_c = \frac{\pi}{d} \left( \frac{K_1}{\chi_a} \right)^{1/2}$$

$H$  is then rapidly decreased to a value  $H_f < H_c$ ; the sample relax to its initial state. In the weak distortion approximation [6], the relaxation time is given by

$$\tau^{-1}(H_f) = \frac{2\chi_a}{\gamma_1} (H_c^2 - H_f^2).$$

Thus, plotting  $\tau^{-1}$  for several values of  $H_f$ , the slope of the curve gives the value of the twist viscosity coefficient, if  $\chi_a$  is known. This diamagnetic anisotropy has been measured at the Centre de Recherche Paul Pascal for M, P<sub>95</sub><sup>4</sup> and P<sub>95</sub><sup>6</sup> [7]. As the  $\chi_a$  values are very close for the solvent and the polymers, we may neglect the effect of the solute in the dilute regime, and use, for solutions at concentration  $\Phi$ ,  $\chi_a(\Phi) = \chi_a(0)$ . In these circumstances, we estimate that  $\gamma_1(\Phi)$  is determined with an accuracy better than  $5 \times 10^{-2}$ .

From the  $\tau^{-1}(H_f)$  plot, it is possible to obtain the values of the splay elastic constant,  $K_1(\Phi)$ , via  $H_c$ , if one measures the thickness of the sample ( $d \approx 100 \mu$ ). This was done using a high accuracy ( $\approx 1 \mu$ ) micrometer; but the determination of the liquid crystal thickness requires several measurements (total cells and each glass slide); so that, on the whole, the uncertainty in the  $K_1$  values is of the order of  $10^{-1}$ .

To summarize, the  $K_1$  and  $\gamma_1$  values were measured for the pure compound M and for all the mixtures indicated in table II, and for several temperatures covering the nematic range of these systems. We generally analyse the data as a function of the reduced temperature  $T_R = T/T_c(\Phi)$ , which is related to the order parameter  $S$  of the mesomorphic phase.

## 2. Experimental results

**2.1 SPLAY ELASTIC CONSTANT  $K_1$ .** — In figure 2 we show a typical example of the variation of  $K_1(\Phi)$  with reduced temperature  $T_R$ , for different polymer (P<sub>95</sub><sup>4</sup>) concentrations. We observe that there is no systematic difference between the pure compound and the solutions. It appears to be a reasonable result considering both the low concentrations we used, and the fact that  $K_1$  values are not drastically different in M and P<sub>N</sub><sup>n</sup> [8].

## 2.2 TWIST VISCOSITY COEFFICIENT $\gamma_1$ .

**Pure solvent M.** — This presents a classical behaviour; the  $\gamma_1$  values are of the same order of magnitude as measured in other l.m.w. nematics, and the dependence on reduced and absolute temperature is well fitted by the empirical law proposed by J. Prost [9]

$$\gamma_1 \propto \chi_a(T_R) \cdot \exp W/T \quad (1)$$

where  $W = 4500$  K.

**Solutions M + P<sub>N</sub><sup>n</sup>.** — The  $\gamma_1$  values are systematically and significantly increased by addition of polymer, even at very low concentration. For instance,  $\Delta\gamma_1/\gamma_1$  increased by about 20 % for  $c = 2$  %, for the polymer P<sub>95</sub><sup>6</sup>. On the whole,  $\Delta\gamma_1$  increases with  $\Phi$ , and when the temperature is lowered.

We undertake a detailed analysis of this effect as a function of the relevant parameters of these systems, i.e. the total chain length  $N$ , the spacer length  $n$ , and the order parameter  $S$ .

We have first to extract, from the directly obtained experimental data, the change in the twist viscosity coefficient between the pure solvent and the different solutions, for the same value of the nematic order parameter, or, equivalently, for the same value of the reduced temperature  $T_R$ ; indeed, this quantity has an intrinsic physical meaning. This is not obvious, as the transition temperature depends on  $\Phi$  (cf. Table II) and as  $\gamma_1$  depends both on  $T_R$ , via  $\chi_a(T_R)$  and on the

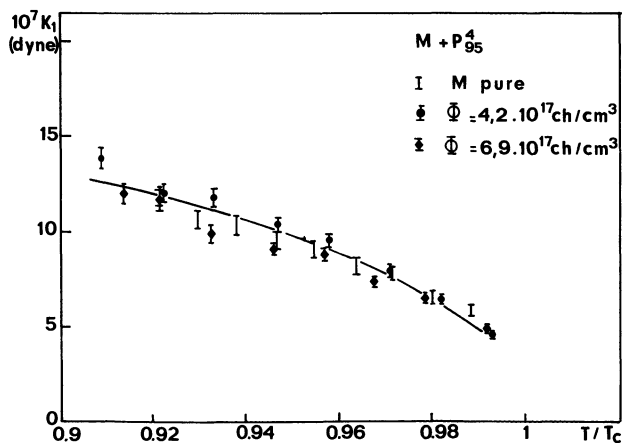


Fig. 2. — Variation of the splay elastic constant,  $K_1$ , as a function of the reduced temperature for different polymer concentrations (P<sub>95</sub><sup>4</sup>).

absolute temperature  $T$ , via the Arrhenian exponential term (cf. Eq. (1)).

Therefore, for each value of the concentration  $\Phi$  and each value of the reduced temperature  $T_R = T/T_c(\Phi)$ , we define the increase in viscosity by

$$\delta\gamma_1(\Phi, T_R) = \gamma_1(\Phi, T_R) - \tilde{\gamma}_1$$

where  $\tilde{\gamma}_1 = \gamma_1(0) \frac{\exp(W/T_{\text{sol}})}{\exp(W/T_{\text{pure}})}$  and where  $T_{\text{sol}}$  and  $T_{\text{pure}}$  are the absolute temperatures corresponding to the same value of  $T_R$  for, respectively, the solution ( $\Phi$ ) and the pure solvent.

We thus verify that  $\delta\gamma_1(\Phi)$ , in the investigated range of concentrations, varies linearly with  $\Phi$ . As this linear dependence corresponds to a situation where the objects are not interacting, this is a good test of the validity of our data analysis. Moreover, this allows us to eliminate the concentration dependence, and to deal now with the ratio  $\delta\gamma_1(\Phi)/\Phi$ , which contains the total physical information.

Finally, to take into account the classical absolute temperature dependency of the friction coefficients, we use the reasonable hypothesis that  $\delta\gamma_1$  presents the same Arrhenian variation as  $\gamma_1(0)$  and consider the quantity

$$A = \delta\gamma_1(\Phi)/\Phi \cdot \exp(W/T). \quad (2)$$

$A$  varies only with the order parameter (or  $T_R$ ) and the characteristics of the polymer, namely  $N$  and  $n$ . All our results may then be summarized by figure 3, where we plotted  $A(T_R, N, n)$  versus  $T_R$  for the systems we studied ( $P_{50}^6$ ,  $P_{95}^4$ ,  $P_{95}^6$ ). In all these cases,  $A$  decreases with the order parameter; notice also that  $A$  is higher for the shorter main chain ( $P_{50}^6$ ).

At this stage, we conclude that our experimental data has shown a significant increase of the twist viscosity, proportional to the polymer concentration in the very dilute regime. This increment, which depends both on the chain length and on the spacer

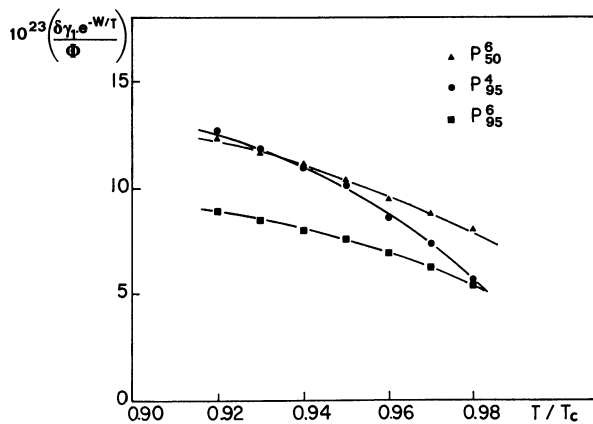


Fig. 3. — Variation of  $A = \delta\gamma_1 e(-W/T)/\Phi$  as a function of the reduced temperature for  $P_{50}^6$ ,  $P_{95}^4$  and  $P_{95}^6$ ;  $\delta\gamma_1$  is the increment of the twist viscosity,  $W$  the activation energy and the number of chains per unit volume.

length, is clearly correlated to the nematic order as shown by the dependence on the reduced temperature.

### 3. Discussion.

As suggested by F. Brochard [3], the increment of the twist viscosity coefficient, when solving a polymeric chain in a nematic medium, has to be related to an anisotropic conformation of the chain. The basic argument is : if the chain has a spherical symmetry, turning on the nematic director  $\mathbf{n}$  has no effect on it ; on the contrary, if the equilibrium shape is anisotropic, the backbone has to rearrange itself to fit to the director orientation, and this cooperative motion induces additional dissipative effects, increasing the value of the viscosity coefficient.

More precisely, F. Brochard described such a situation using an anisotropic dumbbell model : the geometry of the chain is defined by two characteristic sizes,  $R_{\parallel}$  and  $R_{\perp}$ , respectively parallel and perpendicular to  $\mathbf{n}$ ; in the same way, two friction coefficients,  $\lambda_{\parallel}$  and  $\lambda_{\perp}$ , are associated with motions parallel and perpendicular to  $\mathbf{n}$ . One may then derive the expression for the  $\gamma_1$  increment, in the very dilute regime :

$$\delta\gamma_1 = \Phi(k_B T) \tau_R f(R_{\parallel}, R_{\perp}) \quad (3)$$

where  $\tau_R$  is the relaxation time of the chain, given by

$$\tau_R = \frac{1}{(k_B T)} = \frac{\lambda_{\perp} \lambda_{\parallel} R_{\perp}^2 R_{\parallel}^2}{\lambda_{\perp} R_{\perp}^2 + \lambda_{\parallel} R_{\parallel}^2} \quad (4)$$

and  $f(R_{\parallel}, R_{\perp})$  is a geometrical factor

$$f(R_{\parallel}, R_{\perp}) = \frac{(R_{\parallel}^2 - R_{\perp}^2)^2}{R_{\parallel}^2 \cdot R_{\perp}^2}. \quad (5)$$

An equivalent expression of  $\delta\gamma_1$  is

$$\delta\gamma_1 = \Phi \left[ \frac{\lambda_{\perp} \lambda_{\parallel} (R_{\parallel}^2 - R_{\perp}^2)^2}{\lambda_{\perp} R_{\perp}^2 + \lambda_{\parallel} R_{\parallel}^2} \right]. \quad (6)$$

Using for the friction coefficients an Arrhenian temperature depending, with similar activation energy <sup>(1)</sup>, i.e.  $\lambda_{\parallel, \perp} = \lambda_{0\parallel, \perp} \exp^{W/T}$ , we get from equation (6)

$$\delta\gamma_1/\Phi \exp^{W/T} = g(R_{\parallel}, R_{\perp}) \quad (7)$$

with  $g(R_{\parallel}, R_{\perp}) = \frac{\lambda_{0\parallel} \lambda_{0\perp} (R_{\parallel}^2 - R_{\perp}^2)^2}{\lambda_{0\parallel} R_{\parallel}^2 + \lambda_{0\perp} R_{\perp}^2}. \quad (8)$

Notice that the left part of equation (7) is precisely the quantity  $A(N, n, T_R)$  that we directly obtain from experimental data (cf. Eq. (2) and Fig. 3).

The Brochard model thus appears in good qualitative agreement with the observed effects in the twist viscosity behaviour : the linear variation with  $\Phi$ , the

<sup>(1)</sup> This is supported by the experimental fact that Arrhenian laws with the same activation energy has been observed for different nematic viscosity coefficients [10].

exponential dependency with absolute temperature are justified; the increase of  $A(N, n, T_R)$  when  $T_R$  decreases may be clearly related to a more anisotropic shape of the chain for higher order parameter values. We thus conclude that our experimental results do imply that the polymeric coil has a non spherical conformation in the nematic solvent.

*Quantitative discussion.*— It is tempting to go further in the comparison between the experimental and theoretical results; in particular, it is interesting to get an estimation of the magnitude of this geometrical anisotropy, defined by the ratio of the two radii of gyration,  $x = R_{\perp}/R_{\parallel}$ . In the following discussion, we assume  $x > 1$ , which appears physically reasonable (backbone flattened in the direction perpendicular to the nematic axis). However, the determination of  $x$  is not straightforward, as the theoretical expressions (3) or (6) for  $\delta\gamma$ , contain several unknown parameters.

a) Considering the expression given by equation (3), we notice that we may determine  $x$  via  $f(R_{\parallel}, R_{\perp}) = (x^2 - 1)^2/x^2$ , if knowing, besides  $\delta\gamma_1$ , the characteristic time  $\tau_R$ . In principle,  $\tau_R$  may be easily obtained from a complementary measurement by quasi-elastic light scattering technique, being related to the hydrodynamic radius  $R_H$  by  $\tau_R = (\pi\eta/kT)(R_H^3)$ , where  $\eta$  is the value of the viscosity of the medium. In fact, due to the intense light scattering from the orientational fluctuations in the nematic phase, it is difficult to extract the signal due to the diffusion of the coils. Consequently, we measure  $\tau_R$  for the three different polymers  $P_N^n$ , in a conventional solvent (T.H.F.) and renormalize these values in order to take into account the mean value  $\bar{\eta}$  of the liquid crystal shear viscosity. For instance, at  $T_R = 0.97$ , where  $\bar{\eta} = 23$  cp,  $\tau_R$  is estimated to be  $2.2 \times 10^{-5}$  s for  $P_6^{95}$ . The corresponding value of  $x = 1.26$ . In the case of  $P_6^{50}$ , in the same conditions, we get  $x = 1.58$ . We have checked that the order of magnitude of the anisotropy (more than 20 %) is not significantly affected if we take into account a large uncertainty, of the order of 50 %, on the  $\tau_R$  value.

We have to underline that this is indeed a large effect. This would allow a direct determination of the difference between the two main axis by measuring respectively  $R_{\parallel}$  and  $R_{\perp}$  in a small angle X-ray or neutron scattering experiment. The present situation is very different from the case studied by Dubault *et al.* [11] for conventional flexible polymers dissolved in a nematic medium; in that case, a very weak anisotropy ( $x < 1.05$ ) detected by N.M.R., was largely beyond the experimental accuracy in the determination of radii of gyration. This supports the idea [12] that, contrary to the present case, the nematic order is locally destroyed when non-mesogenic polymers are dissolved in a liquid crystal.

b) Besides the order of magnitude of  $x$ , it is interesting to determine its behaviour when varying the order parameter and the characteristics of the polymers. This was done by using equations (7, 8)

with the simplified hypothesis that  $\lambda_{0\parallel} = \lambda_{0\perp}$ , and that the volume for the backbone keeps contact when varying the temperature ( $R_{\perp}^2 R_{\parallel} = V_0$ ). We may then express  $g(R_{\parallel}, R_{\perp})$  in equation (8) as

$$G(x) = \lambda_0 V_0 x^{-4/3} (1 - x^2)^2 / (1 + x^2).$$

Calculating the numerical factor ( $\lambda_0 V_0$ ) for each polymer from the values obtained for  $x$  in a), and fitting  $G(x)$  with the experimental  $A(T_R, N, n)$  data, we obtain the variation of  $x = R_{\perp}/R_{\parallel}$  as a function of the reduced temperature in all three cases.

The results are plotted in figure 4. As expected, the anisotropy ratio increases with three order parameters, in a very similar way for the three polymers. Comparing now between them, we observe that, for a same chain length ( $N = 95$ ), the effect is more pronounced for the shorter spacer ( $n = 4$ ), that may be easily understood as indicating a stronger coupling between the backbone and the nematic order. The most unexpected result is the dependency with  $N$ : the fact that  $x$  is larger for  $P^{50}$  than for  $P^{95}$  is not easy to interpret, and would observe to be checked by a more direct measurement. Notice, however, that in the framework of the Brochard model, the more pronounced anisotropy for the smaller chain length is evidenced by the experimental values of the increment of the viscosity (cf. Fig. 3) and, in that way, is largely independent of the approximations we use in calculating  $R_{\perp}/R_{\parallel}$ .

### 3. Conclusion.

This experimental study of the splay elastic constant  $K_1$  and the twist viscosity coefficient  $\gamma_1$  in dilute solutions of mesomorphic side chain polymers in a nematic solvent shows a large effect in the dissipative property, while the elastic energy keeps unchanged. The dependency of the viscosity increment with concentration and temperature is in good agreement with a model implying an anisotropic conformation of the polymeric backbone. In the framework of this interpretation, we have determined the order of magnitude of the

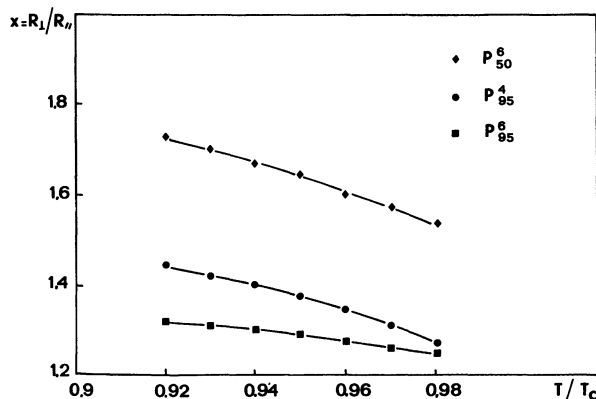


Fig. 4. — Variation of the anisotropy ratio,  $x = R_{\perp}/R_{\parallel}$ , as a function of the reduced temperature for  $P_{50}^6$ ,  $P_{95}^4$  and  $P_{95}^6$ .

ratio of the two characteristic sizes of the coil. If this estimation is correct, the difference between  $R_{\perp}$  and  $R_{\parallel}$  is large enough to be tested by a small angle diffusion technique, within the current accuracy obtained in the determination of radii of gyration.

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