5020 Macromolecules 1990, 23, 5020-5024

Flory's Parameters in Solutions of Liquid Crystalline Side-Chain Polymers in Low Molecular Weight Liquid Crystals

G. Sigaud,* M. F. Achard, F. Hardouin, C. Coulon, H. Richard, and M. Mauzac

Centre de Recherche Paul Pascal, Château Brivazac, Université de Bordeaux I, F-33600, Pessac, France

Received December 12, 1989; Revised Manuscript Received April 23, 1990

ABSTRACT: From the measurement of the critical temperatures at the consolute point in binary solutions of different fractions of a side-chain liquid crystalline polymer in a liquid crystalline solvent we obtain the first evaluation of Flory's interaction parameter in the isotropic and nematic phases. We show that the modification of the solubility from the isotropic to the anisotropic phase results simply from a coupling with the nematic orientational order parameter. The calculation of the binodals from Flory's equation offers a remarkable agreement with the experimental curves of solubility.

Introduction

Many papers deal with the behavior of a polymer chain, either liquid crystalline (LC)[1-3] or not,[4-7] in a nematic solvent of low molecular weight (LMW). Peculiarly, many examples of nematic–nematic phase separation have been reported in solutions of a side-chain LC polymer in a LMW nematogen.[8-13]

However, one of the main goals of the study of polymer solutions is the determination of the interaction constant introduced by the Flory–Huggins theory characterizing the compatibility of the polymer–solvent couple.[14] To our knowledge no experimental work on liquid crystalline solutions has provided the value of this parameter in an anisotropic medium since the different techniques leading to these interaction parameters generally require prohibitive amount compared to the limited availability of liquid crystalline materials.

In this study we have used a technique of determination of this parameter applied long ago by Shultz and Flory[15] based on the measurement of the critical temperature T_C at the consolute point as a function of the degree of polymerization, x. This has been made possible owing to the advantages of the so-called "contact method". (A brief sketch of this technique is given in the Experimental Section. A more detailed description can be found in ref 11.)

In previous works we have shown why this method is well suited to the determination of this critical temperature T_C in solutions of side-chain liquid crystalline polymers with LMW liquid crystalline solvents.[11] We used widely this property to describe the qualitative dependence of this parameter on chemical changes in the polymer as well as in the solvent.[12,13]

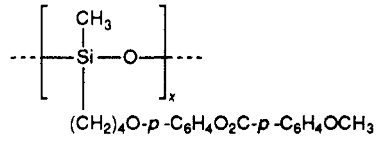
The major achievement of this technique lies in the consumption of very small quantities of compound. The measure of the critical temperatures in a set of well-defined fractions of a LC side-chain polymer with various x thus becomes possible and consequently the determination of the interaction parameters.

The second interest of this work arises from the type of solutions that we study: switching from phase separations occurring in the isotropic state to phase separations occurring in the nematic state with the same LC polymer is easy to perform in a family of homologous LC solvents. The modifications of the interaction parameters from the disordered state to the ordered one can thus be evidenced.

Experimental Section

Three fractions were collected from gel permeation chromatography (GPC) carried out on a commercially available poly(methylhydrogenosiloxane) sample from Merck with an average degree of polymerization of 35. The GPC system consists of a Biobeads SX1 column (35 cm long × 26 mm i.d.). The flow rate is uniform (0.5 cm^3·min^{-1}), and toluene is used as eluent. The volume of injection is 5 cm^3 at a weight concentration of 20%. The molecular weights of the different fractions (Table I) are determined by analytical GPC and confirmed by 270-MHz ^{1}H NMR for the low masses. The analytical GPC is performed by a system of four Touzart & Matignon columns (60 cm long) with various porosities (50, 100, 100, and 500 Å). A uniform flow rate (1.5 cm^3·min^{-1}, toluene as eluent) is maintained through a high-pressure pump. The detector is a differential refractometer. A plot of the volume of retention versus the logarithm of the molecular weight for a set of linear and cyclic oligodimethylsiloxanes provides a linear calibration curve. In all the fractions the molecular weight dispersion is very low ($M_w/M_n < 1.1$).

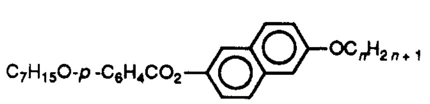
The fixation of the mesogenic groups on the siloxane backbone through a standard hydrosilylation reaction was performed on the three fractions and on an additional commercial poly(methylhydrogenosiloxane) of higher mass (Petrarch, $x = 70$, $M_w/M_n < 1.1$), which is used without further fractionation. The resulting compounds have the following formula:



$$\left[\cdots\mathrm{Si}(\mathrm{CH_3})\big((\mathrm{CH_2})_4\mathrm{O}\text{-}p\text{-}\mathrm{C_6H_4O_2C}\text{-}p\text{-}\mathrm{C_6H_4OCH_3}\big)\text{—O}\cdots\right]_x$$

$x = 70, 41, 32, 18$

The LMW solvents were chosen so that the critical temperatures could be observed for the series of polymers either in the nematic phase or in the isotropic phase. As indicated in the Introduction, this result is simply obtained by varying the length of one of the aliphatic chains in the following compounds:



In the following we characterize each solvent by its total aliphatic carbon content $N = 13, 14, \ldots$: for $N = n + 7 = 13, 14$, the phase separation occurs in the nematic phase (Figure 1a); for $N = n + 7 = 17, 18, 19$, the phase separation occurs in the isotropic phase (Figure 1b).

* To whom correspondence should be sent.

0024-9297/90/2223-5020$02.50/0 © 1990 American Chemical Society

Table I
Degree of Polymerization x of the Different Fractions

fraction	x by GPC	x by ^{1}H NMR
1	18	18
2	32	33
3	41	

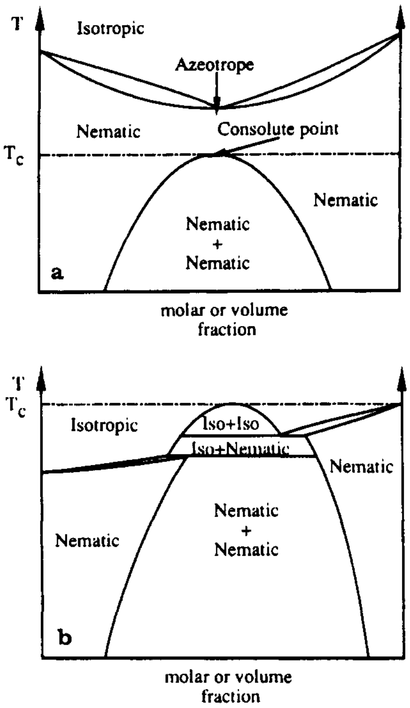


Figure 1. Schematic phase diagrams showing typical topologies for binary mixtures of a side-chain LC polymer in a LMW liquid crystal (the location of the consolute point has been moved to ease drawing: the critical concentration is actually strongly shifted toward low concentration in polymer, $\varphi_{\rm pol} \approx 0.1$).

Table II
Critical Temperatures (°C) for the Different Fractions in the Different Solvents[a]

	x			
N (solvent)	18 ± 1	32 ± 1	41 ± 2	70 ± 3
13		70 ± 1	73.5 ± 1	84 ± 1
14		94.5 ± 1	98.5 ± 1	107 ± 1
17		134 ± 1	146 ± 1	175 ± 1
18		160 ± 1	168 ± 1	205 ± 1
19	122 ± 1	178 ± 1	192 ± 1	220 ± 1

[a] For N = 15 and 16 the phase separation occurs in the nematic–isotropic two-phase domain and no value of T_C is measurable.

For each pair of solvent and solute we prepare a contact sample: a very small quantity of each component is melted on opposite sides of a cover slip and allowed to flow to come in contact. At that time a slight diffusion of one in the other occurs. This small domain of mixing exhibits all the molar fractions for the binary system, and a microscopic investigation of this portion as a function of temperature provides the thermodynamic characteristics of the phase diagram, especially T_C. The values of T_C are reported in Table II.

Results and Discussion

As usual in polymer–solvent systems, T_C decreases with decreasing degree of polymerization. The Flory–Huggins theory of polymer solutions[16] accounts for this behavior and proposes the following equation to describe the variation of T_C with respect to x:[15]

$$\frac{1}{T_C} = \frac{1}{\Theta}\left[1 + \frac{1}{\Psi}\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right)\right] \qquad (1)$$

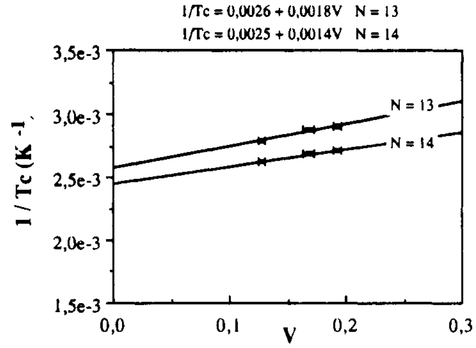


Figure 2. Plots of $1/T_C{}^N$ versus $V = 1/2x + 1/x^{1/2}$; N = 13 and 14 refer to the solvents.

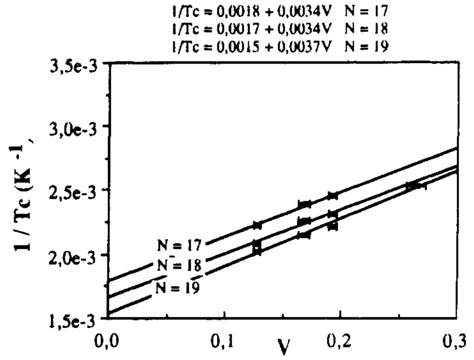


Figure 3. Plots of $1/T_C{}^I$ versus $V = 1/2x + 1/x^{1/2}$; N = 17–19 refer to the solvents.

in which Θ is the Flory temperature, i.e., the critical temperature of mixing of an infinite chain ($x = \infty$), and Ψ is the parameter that accounts in particular for the excess entropy of mixing (see eq 4 below).

We have to consider first that the Flory–Huggins model of a liquid lattice supposes (i) highly flexible, isomolecular nonramified polymers and (ii) equal volume for the molecule of solvent and for the repeat unit of the polymer. These conditions seem to be fairly well fullfilled by our systems: (i) One can reasonably expect that part of the very high flexibility of the linear siloxane main chain is preserved in the polymer substituted by mesogenic groups. (ii) The index of polymolecularity is very close to 1. (iii) The sizes and the chemical nature of the solvents and of the mesogenic side groups are comparable. It seems thus allowable to use the values of Table II and to plot $1/T_C$ as a function of $V = 1/x^{1/2} + 1/2x$. The resulting curves are presented in Figures 2 and 3. A linear fit shows very good agreement for the five polymer–solvent couples, whether the phase separations occur in the nematic (Figure 2) or in the isotropic (Figure 3) phase: the assumptions made on the validity of Flory's model is thus justified a posteriori. However, one immediately remarks that the slopes are clearly different in each of the two cases.

From these fits we derive the values of Θ and Ψ. The uncertainties that can be attributed to these parameters resulting from the experimental uncertainties on x and T_C (see Table II) are respectively 5 K and 0.1 (however, these values must be considered as maxima owing to the highly systematic way in which the experiments are performed). The interaction parameter χ at 298 K is subsequently calculated from the following expression (see Table III):

$$\chi_T = \frac{1}{2} - \Psi\left(1 - \frac{\Theta}{T}\right) \qquad (2)$$

which can also be considered as the sum of a constant term

Table III
Interaction Parameters Calculated from the Fits in Figures 2 and 3

solvent	Θ, K	Ψ	χ_{298}
13	385	1.44	0.92
14	400	1.79	1.11
17	555	0.53	0.96
18	588	0.50	0.99
19	667	0.42	1.02

and a temperature-dependent term:

$$\chi_T = \left(\frac{1}{2} - \Psi\right) + \left(\Psi\frac{\Theta}{T}\right) \tag{3}$$

It is clear that a difference exists between the parameters characterizing the solutions in the nematic phase and the solutions in the isotropic phase. However, a rigorous comparison implies comparison of the values measured at "constant solvent", which is impossible in practice. Although only three sets of parameters Θ and Ψ are available in the isotropic phase, it makes nevertheless some sense to use a linear fit to approximate their virtual values in the isotropic solution with the solvent $N = 14$ (Figure 4): $\Theta^{\mathrm{I}} \approx 380$ K and $\Psi^{\mathrm{I}} \approx 0.72$ can now be compared to the values in the nematic phase, $\Theta^{\mathrm{N}} \approx 400$ K and $\Psi^{\mathrm{N}} \approx 1.79$.

The temperature Θ appears little affected, although it is worth noting that $\Theta^{\mathrm{N}} - \Theta^{\mathrm{I}} > 0$ but the parameter Ψ differs soundly from one phase to the other. It is then clear that the polymer is less soluble in the nematic phase since the interaction parameters at constant solvent and at 298 K are such that

$$\chi^{\mathrm{I}}_{298} = 0.70 < \chi^{\mathrm{N}}_{298} = 1.11$$

We discuss first the results from a phenomenological point of view in terms of the excess entropy $\Delta S_{\mathrm{mM}}{}^{\mathrm{E}}$ and enthalpy of mixing $\Delta H_{\mathrm{mM}}{}^{\mathrm{E}}$, which can be evaluated from the values of Θ and Ψ.

$$\Delta S_{\mathrm{mM}}{}^{\mathrm{E}} = -R\frac{\delta}{\delta T}(\chi_T T)\varphi_2 = -R\left(\frac{1}{2} - \Psi\right)\varphi_2 \tag{4}$$

$$\Delta H_{\mathrm{mM}}{}^{\mathrm{E}} = -RT^2\frac{\delta}{\delta T}(\chi_T)\varphi_2 = R\Psi\theta\varphi_2 \tag{5}$$

where φ_2 is the volume fraction of polymer in the mixture.

According to Hildebrand, the definition for regular solutions implies that $\Delta H_{\mathrm{mM}}{}^{\mathrm{E}}$ is small compared to RT. For such a regular solution $\Delta S_{\mathrm{mM}}{}^{\mathrm{E}} = 0$. Thus one can see that our results show that a solution of a LC polymer in a LMW liquid crystal in the isotropic state approaches the criterions for a regular solution ($\Delta H_{\mathrm{mM}}{}^{\mathrm{E}} \approx 27R$ and $\Delta S_{\mathrm{mM}}{}^{\mathrm{E}} \approx 2 \times 10^{-2}R$).

In contrast, a similar system in the nematic state is no longer regular but real since $\Delta H_{\mathrm{mM}}{}^{\mathrm{E}}$ is significantly increased ($\Delta H_{\mathrm{mM}}{}^{\mathrm{E}} \approx 72R$) and $\Delta S_{\mathrm{mM}}{}^{\mathrm{E}}$ is no longer negligible ($\Delta S_{\mathrm{mM}}{}^{\mathrm{E}} \approx 0.13R$).

It is interesting to recall that nonregular behaviors have long been observed in *nonmesogenic* polymer–solvent systems, particularly in polar solutions,[14,17] and have been regarded as the consequence of local orientational effects inducing an arrangement of the macromolecular segments that is not purely statistical.

In our systems it is obvious that the nematic orientational order in the nematic phases is responsible for the differences observed among the values of Ψ and Θ measured in the isotropic and in the anisotropic phases. We can try to account for these orientational effects through the addition to Flory's interaction parameter of a coupling term with the nematic order parameter as proposed by Brochard et al.

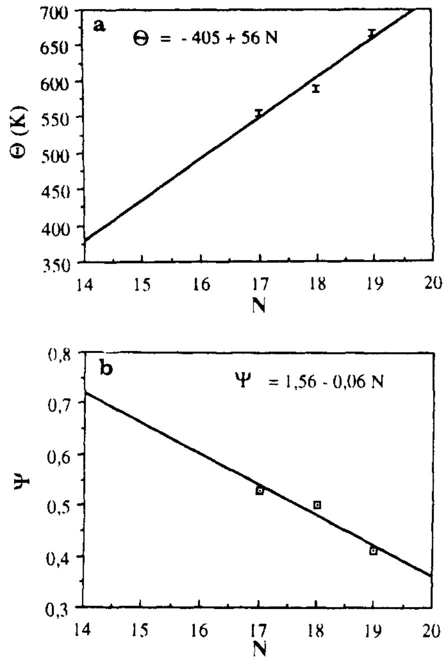


Figure 4. (a) Variation of the Θ^{I} temperature with the aliphatic content of the solvent. (b) Variation of the parameter Ψ^{I} with the aliphatic content of the solvent.

We start from the following form of the interaction parameter derived from Brochard's model[19] applied to one nematic order parameter:[20]

$$\chi_T{}^{\mathrm{N}} = \chi_T{}^{\mathrm{I}} + \frac{\tau S_T{}^2}{T} \tag{6}$$

which is such that, substituting $S_T{}^2$ by its expansion near $T_{\mathrm{C}}{}^{\mathrm{N}}$

$$S_T{}^2 = S_{T_{\mathrm{C}}{}^{\mathrm{N}}}{}^2 + (T - T_{\mathrm{C}}{}^{\mathrm{N}})\left(\frac{\mathrm{d}S^2}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}}$$

and replacing $\chi_T{}^{\mathrm{I}}$ by

$$\chi_T{}^{\mathrm{I}} = \left[\frac{1}{2}\left(1 + \frac{1}{x^{1/2}}\right)^2 - \Psi^{\mathrm{I}}\right] + \Psi^{\mathrm{I}}\frac{T_{\mathrm{C}}{}^{\mathrm{I}}}{T}$$

we obtain an equation of the type expected in Flory's theory similar to eq 3:

$$\chi_T{}^{\mathrm{N}} = \left[\frac{1}{2}\left(1 + \frac{1}{x^{1/2}}\right)^2 - \Psi^{\mathrm{I}} + \tau\left(\frac{\mathrm{d}S^2}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}}\right] + \frac{\Psi^{\mathrm{I}}T_{\mathrm{C}}{}^{\mathrm{I}} + \tau S_{T_{\mathrm{C}}{}^{\mathrm{N}}}{}^2 - \tau T_{\mathrm{C}}{}^{\mathrm{N}}\left(\frac{\mathrm{d}S^2}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}}}{T}$$

The identification term to term with

$$\chi_T{}^{\mathrm{N}} = \left[\frac{1}{2}\left(1 + \frac{1}{x^{1/2}}\right)^2 - \Psi^{\mathrm{N}}\right] + \Psi^{\mathrm{N}}\frac{T_{\mathrm{C}}{}^{\mathrm{N}}}{T} \tag{7}$$

leads to

$$\Psi^{\mathrm{N}} = \Psi^{\mathrm{I}} - \tau\left(\frac{\mathrm{d}S^2}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}}$$

$$\Psi^{\mathrm{N}} = \Psi^{\mathrm{I}} - 2\tau S_{T_{\mathrm{C}}{}^{\mathrm{N}}}\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}} \tag{8}$$

We observe experimentally

$$\chi_T{}^{\mathrm{N}} > \chi_T{}^{\mathrm{I}} \rightarrow \tau > 0 \qquad \text{see (6)}$$

Since S is a decreasing function with T

$$\mathrm{d}S/\mathrm{d}T < 0$$

and thus

$$\Psi^{\mathrm{N}} > \Psi^{\mathrm{I}}$$

The direction of the evolution of Ψ observed experimentally is then consistent with the coupling with S that is considered. We can evaluate this change. For this we transform first τ:

$$\tau = \frac{\chi^{\mathrm{N}}{}_{T_{\mathrm{C}}{}^{\mathrm{N}}} - \chi^{\mathrm{I}}{}_{T_{\mathrm{C}}{}^{\mathrm{N}}}}{S_{T_{\mathrm{C}}{}^{\mathrm{N}}}{}^{2}} T_{\mathrm{C}}{}^{\mathrm{N}} \qquad \text{from (6)}$$

$$\tau = \frac{\frac{1}{2}\left(1 + \frac{1}{x^{1/2}}\right)^2 - \left[\frac{1}{2}\left(1 + \frac{1}{x^{1/2}}\right)^2 - \Psi^{\mathrm{I}}\left(1 - \frac{T_{\mathrm{C}}{}^{\mathrm{I}}}{T_{\mathrm{C}}{}^{\mathrm{N}}}\right)\right]}{S_{T_{\mathrm{C}}{}^{\mathrm{N}}}{}^{2}} T_{\mathrm{C}}{}^{\mathrm{N}}$$

$$\tau = \frac{\Psi^{\mathrm{I}}(T_{\mathrm{C}}{}^{\mathrm{N}} - T_{\mathrm{C}}{}^{\mathrm{I}})}{S_{T_{\mathrm{C}}{}^{\mathrm{N}}}{}^{2}}$$

$$\Psi^{\mathrm{N}} = \Psi^{\mathrm{I}}\left[1 - 2(T_{\mathrm{C}}{}^{\mathrm{N}} - T_{\mathrm{C}}{}^{\mathrm{I}})\frac{1}{S_{T_{\mathrm{C}}}{}^{\mathrm{N}}}\left(\frac{\mathrm{d}S}{\mathrm{d}T}\right)_{T_{\mathrm{C}}{}^{\mathrm{N}}}\right] \qquad \text{from (8)}$$

It must be noted that the difference $\Psi^{\mathrm{N}} - \Psi^{\mathrm{I}}$ is determined mainly by the value of $(\mathrm{d}S/\mathrm{d}T)_{T_{\mathrm{C}}{}^{\mathrm{N}}}$ and consequently tends to zero as the order parameter saturates. To calculate $(1/S_{T_{\mathrm{C}}{}^{\mathrm{N}}})(\mathrm{d}S/\mathrm{d}T)_{T_{\mathrm{C}}{}^{\mathrm{N}}}$ we use the empirical formula proposed by Buka et al.[21] for the evolution of S:

$$S = \left(1 - y\frac{T}{T_{\mathrm{N-I}}}\right)^{z}$$

in which the values of y and z result from a least-squares fit of the thermal variation of the diamagnetic anisotropy in the nematic phase and $T_{\mathrm{N-I}}$ is the temperature of the nematic–isotropic transition. Putting $t = T/T_{\mathrm{N-I}}$

$$\frac{1}{S}\frac{\mathrm{d}S}{\mathrm{d}T} = \frac{1}{T_{\mathrm{N-I}}}\frac{\mathrm{d}\ln S}{\mathrm{d}t}$$

$$\frac{1}{S}\frac{\mathrm{d}S}{\mathrm{d}T} = -\frac{1}{T_{\mathrm{N-I}}}\frac{yz}{1 - yt}$$

Typically $y = 0.998$, $z = 0.2$ (from ref 21); $T_{\mathrm{C}}{}^{\mathrm{N}} = 357$ K, $T_{\mathrm{N-I}} = 362$ K (from ref 22; see below); and $T_{\mathrm{C}}{}^{\mathrm{N}} - T_{\mathrm{C}}{}^{\mathrm{I}} \approx \Theta^{\mathrm{N}} - \Theta^{\mathrm{I}} \approx 20$ K (see above). With $\Psi^{\mathrm{I}}{}_{\mathrm{exp}} = 0.72$, we deduce $\Psi^{\mathrm{N}}{}_{\mathrm{calc}} = 1.73$, which compares very well to the value obtained from the fits: $\Psi^{\mathrm{N}}{}_{\mathrm{exp}} = 1.79$. We can conclude that the coupling with the nematic order parameter explains satisfactorily the lower miscibility in the nematic phase compared to the isotropic phase.

Knowing the thermal variation of χ^{N} (from eq 7), it is also possible to compute the theoretical curves of solubility from the set of equations obtained by equating the chemical potentials of the solvent (and the solute) in the two nematic phases in equilibrium at a given temperature T:

$$\ln(1 - \varphi_2') + \left(1 - \frac{1}{x}\right)\varphi_2' + \chi^{\mathrm{N}}\varphi_2'^2 = \ln(1 - \varphi_2'') + \left(1 - \frac{1}{x}\right)\varphi_2'' + \chi^{\mathrm{N}}\varphi_2''^2 \qquad \text{(9a)}$$

$$\frac{1}{x}\ln\varphi_2' - \left(1 - \frac{1}{x}\right)(1 - \varphi_2') + \chi^{\mathrm{N}}(1 - \varphi_2')^2 = \frac{1}{x}\ln\varphi_2'' - \left(1 - \frac{1}{x}\right)(1 - \varphi_2'') + \chi^{\mathrm{N}}(1 - \varphi_2'')^2 \qquad \text{(9b)}$$

in which φ_2' and φ_2'' are the volume fractions of polymer in each of the separated phases.

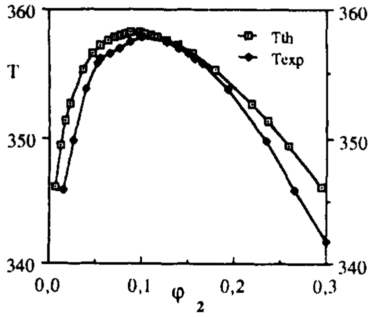


Figure 5. Comparison of the calculated (T_{th}) and experimental (T_{exp}, after ref 22) binodals in the case of the nematic–nematic phase separation.

To avoid heavy calculations, we have applied the method of approximation proposed by Flory.[11,17] Putting

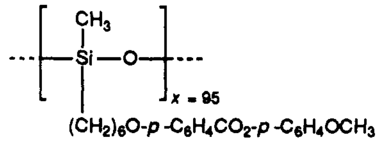
$$\gamma = \varphi_2''/\varphi_2' \qquad (10)$$

and provided that both φ_2' and φ_2'' are small, one obtains the following relationship between γ, φ_2', and x:

$$\frac{\varphi_2'^2}{1 - (\gamma + 1)\varphi_2'} = \frac{12[{}^1/_2(\gamma + 1)\ln\gamma - \gamma + 1]}{x(\gamma - 1)^3} \qquad (11)$$

A value of γ is assumed, and φ_2' is calculated from eq 11, which defines also the value of φ_2'' from (8). This pair of values is injected in one of the equations of set (9) to obtain χ^{N} and finally the value of the corresponding temperature from (7).

To check how the theoretical curve matches with experimental data, it is necessary to establish the phase diagram as a function of known volume fractions of polymer. This heavy work has been made independently by Casagrande et al.[22] for one polymer–solvent system almost similar to the couples that we studied by the contact method and that offers a consolute point in the nematic domain. The polymer is also a poly(methylsiloxane) substituted with slightly different mesogenic groups and degree of polymerization:



$$\cdots\left[\mathrm{Si}(\mathrm{CH_3})\left((\mathrm{CH_2})_6\mathrm{O}\text{-}p\text{-}\mathrm{C_6H_4CO_2}\text{-}p\text{-}\mathrm{C_6H_4OCH_3}\right)\text{—O}\right]_{x = 95}\cdots$$

The LMW solvent is $\mathrm{C_7H_{15}O}$-p-$\mathrm{C_6H_4CO_2}$-p-$\mathrm{C_6H_4OC_6H_{13}}$ and possesses the same aliphatic content as one of the solvents we used ($N = 13$). We have drawn the cloud point curve as a function of the weight fraction of polymer, but since the molecular weight of the solvent (416 g·mol^{-1}) is comparable to the molecular weight of the repeat unit of the polymer (386 g·mol^{-1}), the corrections expected in the case of a change to volume fractions are negligible (<2/100). We then compared in Figure 5 the theoretical curve computed with $x = 95$, $\Psi = 1.44$, and $\Theta = 385$ K (corresponding to $N = 13$ (Table III)) directly with the cloud point curve from Casagrande et al.

The remarkable agreement between the curves is highly surprising since the attempts made so far in *nonmesogenic* solutions to test the validity of eq 9 in their simplest form gave a poor quantitative comparison. We point out that this better agreement is a direct consequence of the enlargement of the parameter Ψ through the coupling with the order parameter which widens the theoretical biphasic domain. In fact, the theoretial curve would even compare better to the experimental data if one admits that the value of Ψ^{N} should be slightly damped as T decreases since $(1/S)(\mathrm{d}S/\mathrm{d}T)$ decreases too as the gap in the nematic–isotropic transition increases.

Conclusion

The values of the interaction parameters in solutions of a nematogenic side-chain polymer and a nematogenic solvent reported in this paper are the very first. They have been obtained by the contact method, which definitely proves its handiness in the study of polymer solutions.

Two results are especially interesting in the analysis of these parameters:

(i) From the comparison between these values in the isotropic and in the nematic phases it turns out that the solubility in the nematic phase is less. A coupling with the orientational order parameter as proposed by F. Brochard in her "first-generation theory"[20] gives a satisfying interpretation of this result and shows that the unsaturation of the order parameter plays an important role in this difference.

(ii) The calculation of the binodals from the Flory–Huggins equations using these parameters agrees well with the experimental data presently available. Whether this is fortuitous or is a characteristic feature of the phase separation in the nematic phase has to be confirmed by additional experiments.

The extension of these studies seems thus valuable in both experimental and theoretical areas.

Acknowledgment. We are greatly indebted to M. Masure and P. Sigwalt for their help in analytical GPC measurements and to Nguyen Huu Tinh for providing the LMW solvents.

References and Notes

(1) Weill, C.; Casagrande, C.; Veyssie, M.; Finkelmann, H. *J. Phys. (Paris)* **1982**, *47*, 887.
(2) Mattoussi, H.; Ober, R.; Veyssie, M.; Finkelmann, H. *Europhys. Lett.* **1986**, *2*, 233.
(3) Finkelmann, H.; Kock, H.-J.; Rehage, G. *Mol. Cryst. Liq. Cryst.* **1982**, *89*, 23.
(4) Kronberg, B.; Bassignana, I.; Patterson, D. *J. Phys. Chem.* **1978**, *82*, 1714.
(5) Dubault, A.; Casagrande, C.; Veyssie, M. *Mol. Cryst. Liq. Cryst. Lett.* **1982**, *72*, 189.
(6) Dubault, A.; Ober, R.; Veyssie, M.; Cabane, B. *J. Phys. (Paris)* **1985**, *46*, 1227.
(7) (a) Dormoy, Y.; Gallani, J. L.; Martinoty, P. *Mol. Cryst. Liq. Cryst.* **1989**, *170*, 135. (b) Dormoy, Y.; Reys, V.; Martinoty, P. *Liq. Cryst.* **1989**, *6*, 409.
(8) Ringsdorf, H.; Schmidt, H. W.; Schneller, A. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 745.
(9) Casagrande, C.; Veyssie, M.; Finkelmann, H. *J. Phys., Lett.* **1982**, *43*, L-371.
(10) Benthack-Thoms, H.; Finkelmann, H. *Makromol. Chem.* **1985**, *186*, 1895.
(11) Sigaud, G.; Achard, M. F.; Hardouin, F.; Mauzac, M.; Richard, H.; Gasparoux, H. *Macromolecules* **1987**, *20*, 578.
(12) Sigaud, G.; Achard, M. F.; Hardouin, F.; Gasparoux, H. *Mol. Cryst. Liq. Cryst.* **1987**, *155*, 443.
(13) Achard, M. F.; Sigaud, G.; Keller, P.; Hardouin, F. *Makromol. Chem.* **1988**, *189*, 2159.
(14) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(15) Shultz, A. R.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 4760, **1953**, *75*, 3888; *J. Polym. Sci.* **1955**, *15*, 231.
(16) For a comprehensive review on polymer solutions, see: Cassasa, E. F.; Berry, C. G. *Comprehensive Polymer Science*; Bevington, A., Ed.; Pergamon: New York, 1989; Vol. 2, Chapter 3, pp 71–120.
(17) Tompa, H. *Polymer Solutions*; Butterworths Scientific Publications: London, 1956.
(18) *Chimie Macromoléculaire*; Hermann: Paris, 1972: (a) Quivoron, C., Vol. 2, Chapter 1, pp 3–63; (b) Sebille, B., Vol. 2, Chapter 2, pp 65–161.
(19) (a) Brochard, F. *C. R. Hebd. Seances Acad. Sci.* **1979**, *289B*, 229. (b) Brochard, F.; Jouffroy, J.; Levinson, P. *J. Phys. (Paris)* **1984**, *45*, 1125.
(20) The use of a single order parameter is experimentally justified by the fact that the critical point in these systems appears to locate close to an azeotrope, i.e., a minimum in the nematic–isotropic equilibrium curve (see Figure 1a and phase diagram in ref 22), at which the order parameters of the solvent and the solute should be equal as stated in ref 19b.
(21) Buka, A.; De Jeu, W. H. *J. Phys. (Paris)* **1982**, *43*, 361.
(22) Casagrande, C.; Guedeau, M. A.; Veyssie, M. *Mol. Cryst. Liq. Cryst. Lett.* **1987**, *4*, 107.

Registry No. N = 13, 129708-43-6; N = 14, 129708-44-7; N = 17, 129733-04-6; N = 18, 129708-45-8; N = 19, 129708-46-9.