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Origin of Thermotropicity in Polymer Liquid Crystals

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ABSTRACT: Viscosity measurements were performed over the temperature range 25-140 °C for fractions of poly(phenylhydroquinone-*co*-terephthalic acid) (PPHT) dissolved in a 1:1 mixture of *o*-dichlorobenzene and *p*-chlorophenol. The objective was to evaluate the temperature coefficient of the persistence length (q) and to extrapolate the axial ratio of the Kuhn link, $2q/d$, to the nematic-isotropic transition temperature, $T_{NI}^\circ = 460$ °C, of PPHT. Here d is the diameter of the chain. The temperature coefficient $\mathrm{d} \ln q/\mathrm{d}T$ is -3.8×10^{-3} °C^{-1}. This is slightly smaller than observed for other thermotropic polymers, but still much larger than observed for flexible polymers. The best estimate of the axial ratio $2q/d$ at T_{NI}° is equal to 4.9. In spite of the long extrapolation involved, this result is consistent with the concept of a temperature-dependent axial ratio attaining, at T_{NI}°, a value which reflects a balance between hard and soft interactions.

Introduction

Early molecular theories of liquid crystallinity emphasized the role of anisotropic attractive (soft)[1] and repulsive (hard) interactions[2,3] in the stabilization of the mesophase of low molecular weight compounds and of rigid rods, respectively. The asymmetric shape of rigid rods is sufficient to cause an entropy-driven transition from the isotropic to the anisotropic phase above a critical value of the axial ratio, X_c, and rod volume fraction, v_2.[2,3] Alternatively, for the more symmetric low molecular weight compounds, the transition is energy-driven by anisotropic attractions of quadrupolar symmetry.[1]

On this basis the term "lyotropic" was applied to systems composed of a rodlike solute and a conventional solvent when the transition is triggered by a change in the concentration of rodlike solute. The term "thermotropic" was instead applied to the low molecular weight compounds when the transition is induced by temperature changes, usually in the bulk (sometimes in very concentrated solutions).

More recent theories[4,5] have surmounted such strict differentiations between the two classes of compounds and recognized that both hard and soft interactions may be operative in all systems. The critical value of the axial ratio for rods below which hard interaction is not sufficient to stabilize the mesophase is predicted to be 3.5 by the virial treatment[2] and 6.4 by the lattice theory.[3] The relative contribution of soft and hard interactions for undiluted systems ($v_2 = 1$) predicted from the lattice model of Flory and Ronca is[5]

$$\frac{XT^*}{T_{NI}^\circ} = T_{NI}^{-1} \tag{1}$$

where T_{NI}° is the nematic-isotropic transition temperature. The strength of soft interactions is characterized by T^*. T_{NI}^{-1} is a reciprocal, reduced, and therefore dimensionless transition temperature. This ratio is predicted to attain the value zero when the axial ratio, X, is greater than 6.4. Under these conditions they predict $T_{NI}^\circ = \infty$; i.e., the mesophase is "absolutely stable" irrespective of soft interactions. However, when the axial ratio is smaller than the critical value, and T_{NI}° falls into the measurable range, its actual value is determined by both X and T^*. For undiluted systems just described, thermotropicity is therefore due to an interplay of hard interactions, described by a $X < X_c$, and soft interactions, described by a $T^* > 0$.

This situation is not necessarily restricted to low molecular weight compounds. Segmented polyesters (e.g., aliphatic esters of 4,4′-dihydroxy-α-methylstilbene[6] or of 4,4′-dihydroxybiphenyl[7]) have an axial ratio of the rigid segment which is usually smaller than 6.4. Even though a partial orientation of the flexible segment may occur within the mesophase of these polymers,[8,9] both soft and hard interactions are used to explain their thermotropicity.[9]

The above concepts can also be extended to interpret thermotropicity when a diluent is present, i.e., in systems which also show lyotropic behavior. According to Warner and Flory,[10] for a given axial ratio the nematic-isotropic transition can be induced by temperature, but only in the close proximity of the critical concentration, v_2'. The critical concentration is smaller when the axial ratio is larger ($v_2' \sim 6.4/X$). A scaled soft interaction, T^*v_2, is assumed to add stabilization to a mesophase primarily stabilized by hard interaction.

In previous papers[11-14] we pointed out that one important consideration is missing in the above theoretical description of thermotropicity. The missing point is the temperature coefficient of the axial ratio. In fact, the temperature coefficient of the persistence length has been found to be unexpectedly large for mesogenic polymers such as poly(*n*-hexyl isocyanate) (PHIC) and cellulose derivatives. The observation of a very large thermotropic effect covering a range of v_2 from 0.2 to 1 for the latter polymers cannot, in fact, be justified in terms of soft interactions. Not only are these predicted to be effective only in a small concentration range close to v_2' but the large side chains of the two polymers cited above prevent the establishment of close contacts between the molecules. The possibility that volume expansion effects, or isotropic interactions, could offer an explanation for these thermotropic effects was ruled out.[14] Moreover, the observation of a finite nematic transition temperature for undiluted polyesters such as substituted poly(*p*-phenylene terephthalates)[15] is also interesting in terms of the above consideration.

Our attempts to determine the axial ratio at T_{NI}° using the temperature coefficient of the persistence length (q) have provided the remarkable result that, for PHIC and cellulose derivatives, the quantity

$$X_k = 2q/d \tag{2}$$

is rather close to the critical axial ratio 6.7 predicted by the lattice treatment of semirigid mesogens using the Kuhn chain model.[12,16] In eq 2, X_k is the axial ratio of the Kuhn segment, and d is the chain diameter. The use of X_k is based on the assumption that the *limiting* behavior of a semirigid mesogen is controlled by the Kuhn segment *rather than by the contour length.* This assumption is made using both the lattice[16] and the virial theory,[17] and

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Table I
Characteristics of Fractions Investigated

fraction	$[\eta]$, mL/g	$\langle M\rangle_w$
F1	350.0	48 500
F3	241.8	30 700
F7	111.3	13 100
F9	58.7	(6070)

for some unexplained reason, the model of the Kuhn chain offers a better approximation to the experimental behavior than that of the more sophisticated wormlike chain.[14] Our results further showed that the large thermotropic effect in the composition range $0.2 < v_2 < 1.0$ for PHIC and cellulose derivatives could satisfactorily be accounted for by the experimentally measured variation of X_k with temperature.

The above results suggest that for PHIC and cellulose derivatives soft interactions are unnecessary or play only a minor role in the thermotropic behavior. $T_{NI}°$ is simply the temperature at which the axial ratio attains the critical value describing purely hard interactions. This interpretation rests entirely on the occurrence of such a critical ratio. Conformational energy effects are involved in the temperature coefficient of X_k, but these have quite a different origin than the asymmetric dispersion forces considered by Maier and Saupe.[1] To explore the validity of the above suggestions for other polymer systems, particularly those for which the chemical structure suggests that soft interactions may be operative, we consider in this paper the temperature coefficient of X_k for a fully aromatic polyester, poly(phenylhydroquinone-*co*-terephthalic acid) (PPHT). This polymer has been shown to exhibit a $T_{NI}°$ in the order of 460 °C[15,18] and a persistence length[18] on the order of 100 Å. The latter indicates that this polymer can be regarded as semirigid, and therefore the analysis based on eq 2 can be applied to it.

Experimental Section

Four PPHT fractions were used, having characteristics collected in Table I. These were obtained[18] from a polymer synthesized using terephthalic acid, phenylhydroquinone diacetate, and Mg catalyst at temperatures between 285 and 350 °C. Fractionation was performed[18] by fractional precipitation from a solution of PPHT dissolved in a 1:1 (w/w) mixture of *o*-dichlorobenzene (*o*-DCB) and *p*-chlorophenol (*p*-CP) using methanol as the nonsolvent. Intrinsic viscosity was determined as a function of temperature between 25 and 140 °C (±0.1 °C) by using a No. 50 Cannon-Ubelhode dilution viscometer equipped with a modified system,[19] allowing measurements in an inert argon atmosphere. Stock solutions for each fraction ranged between 0.26 and 1.08 g/dL. *p*-CP was vacuum distilled, and *o*-DCB was analytical grade. Flow times for the solvent exceeded 100 s at each temperature. The thermal expansion coefficient for *o*-DCB ($\alpha = 8.5 \times 10^{-4}$ °C^{-1}) was used to estimate the small correction of the solution concentrations at temperatures above 25 °C.[20] Flow times were measured in duplicate at each temperature, beginning at 60 °C. Flow times remeasured at 60 °C, after measuring flow times at 100 and 140 °C, agreed with the initial average found at 60 °C, indicating a lack of polymer degradation.

The density (ρ_2) of polymer, which had been dissolved and reprecipitated, was determined by buoyancy using a mixture of chloroform and *o*-dichlorobenzene. The density of the liquid mixture was determined by picnometry.[13]

Results and Discussion

Figure 1 and Table II illustrate the molecular weight dependence of the intrinsic viscosity of PPHT between 25 and 140 °C. The experimental dependence of $[\eta]$ upon $\langle M_w\rangle$ at 25 °C (Figure 1) is represented by

$$[\eta] = 3.0 \times 10^{-4}\langle M_w\rangle^{0.869} \qquad (3)$$

which was previously reported by Krigbaum and Tanaka.[18]

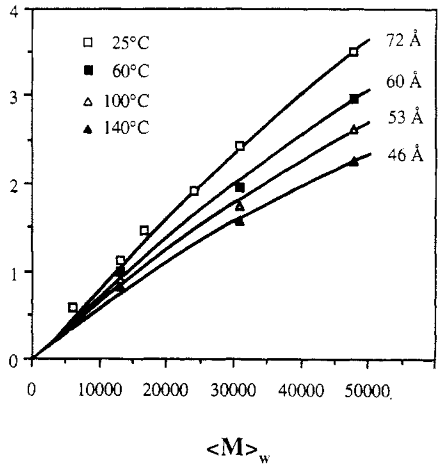

Figure 1. Experimental variation of the intrinsic viscosity with molecular weight for PPHT in 1:1 *o*-DCB/*p*-CP at the indicated temperatures. The full curves represent the $[\eta]$–M_w dependence calculated from the Yamakawa–Fujii treatment using $d = 5.5$ Å and $M_L = 24.5$ Å^{-1}, with the resulting best fit values of the persistence length as indicated. Data at 25 °C include additional fractions investigated by Krigbaum and Tanaka.[18]

Table II
Temperature Dependence of the Intrinsic Viscosity of PPHT Fractions in 1:1 *o*-DCB/*p*-CP

	$[\eta]$, mL/g			
T, °C	F1	F3	F7	F9
25	350	242	111	58.7
60	296	195	100	42.2
100	263	175	90.0	38.0
140	225	156	80.7	35.1

Note, however, that the molecular weight of the lowest fraction (F9) was not measured by light scattering and that eq 3 is strictly valid in the molecular weight range 13000–48500. Thus, the molecular weight deduced for F9 using eq 3 is subject to some uncertainty, and on this account, this fraction was not included in evaluating the persistence length. The exponent of the Mark–Houwink equation decreases from 0.87 at 25 °C to 0.79 at 140 °C.

The full curves in Figure 1 are calculated by using the relationship of Yamakawa and Fujii (Y–F):[21]

$$[\eta] = \frac{\Phi L'^{3/2}}{\lambda^3 M} \qquad (4)$$

where $L' = \lambda M/M_L$ is the reduced contour length, with M_L being the mass per unit length and $\lambda = (2q)^{-1}$. Φ is a function of L' and of the reduced diameter d' ($=\lambda d$) calculated by Yamakawa and Fujii.[21] M_L was taken equal to 24.5 daltons/Å, corresponding to the molecular weight of the repeat unit (316 g/mol) and a residue vector $l_o = 12.9$ Å, as calculated by Herman et al.[22] As in previous work,[12,13] we have used the following equation to calculate the molecular diameter:

$$d = [M_L/(\rho_2 N_A)]^{1/2} \qquad (5)$$

where N_A is Avogadro's number, and ρ_2 is the polymer density (1.362 g/mL). The diameter obtained by using eq 5 is $d = 5.5$ Å. Values of q derived from the Y–F treatment with $d = 5.5$ Å and $M_L = 24.5$ Å^{-1} are in Table III. Since this d value is considerably smaller than the value, 10 Å, used by Krigbaum and Tanaka[18] to derive the persistence length at 25 °C, we consider in more detail the geometry of the phenyl-substituted hydroquinone unit in Figure 2. The four projections shown were calculated from normal bond angles, bond distances, and the atomic radius of hydrogen (0.31 Å).[23] The average of these four projections

Table III
Persistence Length (Å) Temperature-Dependence Data for PPHT in 1:1 *o*-DCB/*p*-CP

T, °C	Yamakawa–Fujii; q		Bohdanecky treatment			optical anisotropy;[a] q
	d = 5.5	d = 7.0	q	B_η	A_η	
25	72	68	66	0.69	33.5	87
60	60	57	57	0.74	37.0	
100	53	50	51	0.78	35.5	
140	46	43	44	0.84	33.8	
10^3(d ln q)/dT, °C^{-1}	-3.8	-3.9	-3.5			

[a] From ref 18.

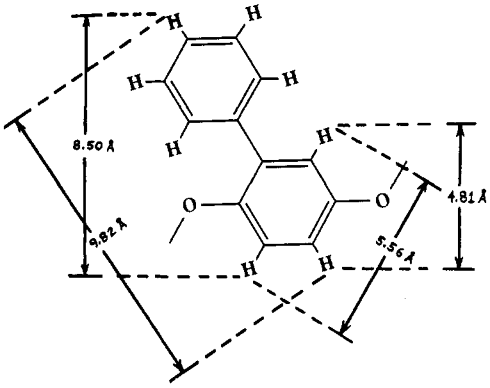

Figure 2. Estimate of the average diameter of PPHT using typical bond lengths and the atomic radius of hydrogen. The average of the four projections shown is 7.17 Å.

is 7.17 Å. This estimate for d, being between the two values mentioned above, led us to consider an alternative method to derive q and d.

Equation 5 assumes a square cross section and assigns to d the value of the side of the square. If we assume a circular cylinder, eq 5 is replaced by

$$d = [4M_L/\pi\rho_2 N_A]^{1/2} \qquad (6)$$

This equation yields d = 6.2 Å, which lies between the value obtained from eq 5 and the value, 7.17 Å, deduced from models.

The Bohdanecky treatment[24] is an approximate version of the Y–F theory, which has the advantage that prior knowledge of the diameter is not required. The relationships are

$$(M^2/[\eta])^{1/3} = A_\eta + B_\eta M^{1/2} \qquad (7)$$

$$A_\eta = A_0 M_L \Phi_\infty^{-1/3} \qquad (8)$$

$$B_\eta = 1.05\Phi_\infty^{-1/3}(2q/M_L)^{-1/2} \qquad (9)$$

where Φ_∞ is the limiting value of Φ ($\Phi_\infty = 2.86 \times 10^{23}$) for nondraining coils in the limit of infinite molecular weight and A_0 is a function of d' given by Bohdanecky.[24] In Figure 3, $(\langle M_w\rangle^2/[\eta])^{1/3}$ is plotted versus $\langle M_w\rangle^{1/2}$ at each temperature. The slopes and intercepts, B_η and A_η, are given in Table III. Persistence lengths calculated from the slope at each temperature using a constant value of M_L = 24.5 Å^{-1} are given in the fourth column of Table III.

To estimate the diameter, Bohdanecky[24] suggests the following equation based on the assumption that the hydrodynamic volume occupied by 1 g of the wormlike cylinder is equal to the partial specific volume, $\bar{v}_2$, of the polymer:

$$d'^2/A_0 = (4\Phi_\infty/1.215N_A)(\bar{v}_2/A_\eta)B_\eta^4 \qquad (10)$$

Once $(\bar{v}_2/A_\eta)B_\eta^4$ is calculated using ρ_2^{-1} as an estimate for the partial specific volume of PPHT at 25 °C, d' can be evaluated by the dependence of d'^2/A_0 on d' using eq 11 or 12.

$$\log (d'^2/A_0) = 0.173 + 2.158 \log d' \qquad (d' \leq 0.1) \qquad (11)$$

$$\log (d'^2/A_0) = 0.795 + 2.78 \log d' \qquad (0.1 \leq d' \leq 0.4) \qquad (12)$$

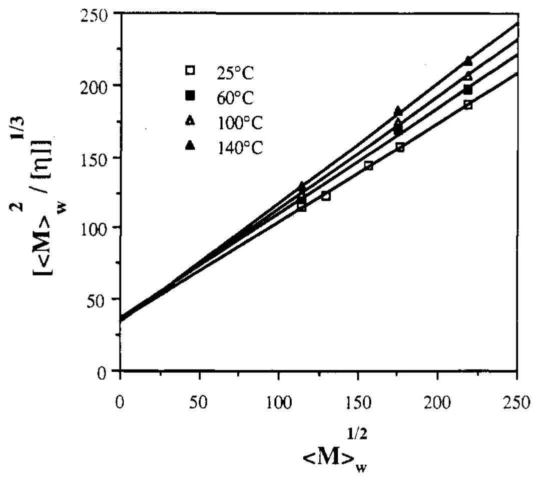

Figure 3. Plot of $(\langle M_w\rangle^2/[\eta])^{1/3}$ versus $\langle M_w\rangle^{1/2}$ according to the treatment of Bohdanecky[24] using the data from Figure 1.

Table IV
Axial Ratio–Temperature Data for PPHT in 1:1 *o*-DCB/*p*-CP

method	d, Å	T d ln X_k/dT	X_k at $T_{NI}°$	T*
[η], Y-F	5.5	-1.35	4.9	217
[η], Y-F	7.0	-1.38	3.5	534
[η], Bohdanecky	7.0	-1.24	4.1	384
optical anisotropy	7.0	-1.33	4.8	224

At 25 °C, d' is 0.0515, yielding a value of 6.8 Å for d using the corresponding values from Table III. This value for d is in good agreement with the geometrical considerations and the value deduced from eq 6. We have therefore evaluated the effect of an increase of d from 5.5 to 7 Å on the results of the Y–F treatment. The results are shown in column 3 of Table III. Values of q obtained with the Y–F treatment using d = 7 Å and M_L = 24.5 Å^{-1} are similar to those obtained with the Bohdanecky treatment and slightly smaller than those obtained according to Y–F using d = 5.5 Å. Our q values, which range from 66 to 72 Å, are larger than those reported from viscosity measurements by Krigbaum and Tanaka,[18] q = 60 Å, due primarily to their use of a diameter which is larger than the values reported here. The reported q values are not corrected for the temperature variation of d since this revision introduces negligible effects.[14]

Also shown in Table III is the value of q determined by Krigbaum and Tanaka[18] from optical anisotropy at 25 °C. This value is somewhat larger than the values derived from intrinsic viscosity. (Krigbaum and Tanaka[18] have also reported an exceptionally large q value, 150 Å, from diffusion measurements at 25 °C.) The Y–F theory for intrinsic viscosity has often been shown to yield lower values of q than those obtained using alternative approaches.[11,14,25] However, in the case of (hydroxypropyl)cellulose, q_{YF} obtained from the Y–F treatment was similar to q_{BD} derived from the Benoit–Doty treatment of light scattering data for wormlike chains and to q_{CL}, the coil limiting value described by eq 9.[11] Saito[25] pointed out that the frequent observation that $q_{YF} < q_{BD}$ may reflect the neglect of free draining effects in the Y–F theory. Excluded volume effects are, in fact, generally negligible for the semirigid polymers.[11,25–27]

Table V
Summary of Temperature Dependence of Persistence Lengths and Axial Ratios at $T_{NI}°$

system	ref	$q_{25°}$, Å	$T_{NI}°$, °C	d ln q/dT, deg^{-1}	T d ln q/dT	X_k at $T_{NI}°$	T*, K
PPHT/*o*-DCB/*p*-CP	this work[a]	72	460	−0.0038	−1.35	4.9	217
PHIC/1-CN	13 (14)	95	180	−0.011	−3.7	4.1	235
PHIC/Tol	12 (14)	310	180	−0.011	−3.6	6.8	0
HPC/DMAC[b]	11 (14)	70	210	−0.0050	−1.7	4.8	160
APC/DMPh[c]	28 (14)	60	182	−0.0045	−1.6	4.5	170

[a] Y–F, d = 5.5 Å, M_L = 24.5 daltons/Å. [b] (Hydroxypropyl)cellulose/*N*,*N*-dimethylacetamide. [c] (Acetoxypropyl)cellulose/dimethyl phthalate.

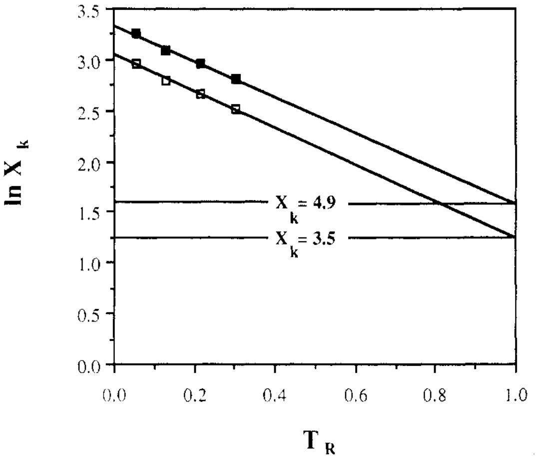

Figure 4. Temperature dependence of the axial ratio of the Kuhn segment for PPHT in 1:1 *o*-DCB/*p*-CP. T_R is a reduced temperature, $T_R = T/T_{NI}°$. The extrapolated value of X_k at $T_{NI}°$ is indicated. (■) Values of q derived by Y-F theory with M_L = 24.5 Å^{-1} and d = 5.5 Å. (□) Values of q derived by Y-F theory with M_L = 24.5 Å^{-1} and d = 7.0 Å.

Selected temperature variations of the axial ratio of the Kuhn segment defined in eq 2 are calculated from data in Table III and plotted in Figure 4. The data are plotted using a reduced temperature $T_R = T/T_{NI}°$ with $T_{NI}°$ = 460 °C. The latter figure is an average of $T_{NI}°$ temperatures previously reported.[15,18] $T_{NI}°$ = 475 °C was reported by Krigbaum et al.[15] using a DSC heating rate of 40 °C/min for unfractionated PPHT having [η] = 1.70 dL/g. Krigbaum and Tanaka[18] using a heating rate of 10 °C/min reported $T_{NI}°$ = 450 °C for a PPHT fraction having [η] = 1.9 dL/g. We do not have data exhibiting an effect of molecular weight on $T_{NI}°$. The molecular weight of the latter fraction, 24 000, corresponds to a chain with a contour length $L \sim 1000$ Å equivalent to ~8 Kuhn segments. The asymptotic behavior of a semirigid chain should nearly be reached under these conditions.[14]

The results of the extrapolation of X_k at $T_{NI}°$ corresponding to the data in Table III are given in Table IV. For the optical anisotropy data we assumed a temperature coefficient equal to the average of the coefficients obtained from the viscosity data. The diameters have not been corrected for their temperature variation since this effect has been shown to introduce only a small correction (~ 4%) to the intercept obtained without this correction.[14] In view of the long extrapolation from 140 to 460 °C, the value of the intercept at T_R = 1 must, in any case, be viewed with reservation. A change of diameter from 5.5 to 7 Å does not produce large effects on the value of q (Table III) but significantly affects the $2q/d$ ratio. For consistency with other published data,[11-14] we place more emphasis on the value 4.9, obtained by using the Y–F treatment and the diameter from eq 5. This value is gratifyingly consistent with the persistence length obtained from optical anisotropy using the larger diameter. It is remarkable that the axial ratios at T_R do not largely scatter from the range (4.1–6.8) observed for PHIC and cellulose derivatives. A summary of the data, including the present study, is reported in Table V.

Since axial ratios at $T_{NI}°$ are smaller than the value predicted by the lattice theory for purely hard interactions, a contribution due to soft interactions is suggested. Values of T* were calculated using the plot of $XT^*/T_{NI}°$ (cf. eq 1) versus the axial ratio at $T_{NI}°$ given by Flory and Ronca.[5] The T* values, included in Tables IV and V, appear to be somewhat larger than those obtained for PHIC and cellulose derivatives and suggest that a contribution from soft interactions may occur in the aromatic polyester considered here. Note, however, that the large $T_{NI}°$ for PPHT can also be justified in terms of the present model on the basis of a d ln q/dT not as large as for the other systems previously investigated.

In conclusion, the absolute value of d ln q/d ln T for PPHT is somewhat larger than expected for a classical wormlike chain[29,30] and considerably larger than that observed for a conventional flexible polymer such as polyethylene (−0.46).[31] The coefficient is smaller but comparable to that observed for other mesogenic polymers such as PHIC and cellulose derivatives which exhibit lower $T_{NI}°$ values. The value of the axial ratio at $T_{NI}°$ of PPHT is similar to those observed for PHIC and cellulose derivatives and are still within a range compatible with the existence of a critical axial ratio describing purely hard interactions. In fact, the theoretical value of the critical axial ratio is subject to some indeterminacy. The value 6.7 was reported for the Kuhn chain,[12] and inclusion of free volume in the lattice treatment[32] would somewhat increase[14] the latter value. However, a value of 3.5 is predicted for hard rods by the virial theory. On the other hand, application of the Flory–Ronca theory to the present data yields a T* value somewhat larger than for the other polymer systems investigated and not inconsistent with T* reported for low molecular weight mesogens.[32] Therefore, it is possible that at $T_{NI}°$ the temperature-dependent axial ratio has attained a value *smaller* than the critical value due to the existence of a contribution from soft interactions. In order to independently assess the occurrence of soft interactions, it would be interesting to investigate whether a segmented polymer including the repeat unit of PPHT and a flexible spacer[9] exhibits a mesophase consistent with the value of T* reported here.

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Registry No. (Phenylhydroquinone diacetate)(terephthalic acid) (copolymer), 67203-16-1; (phenylhydroquinone diacetate)(terephthalic acid) (SRU), 67256-36-4.

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Molecular Weight Dependence of the Second Virial Coefficient for Flexible Polymer Chains in Two Dimensions

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ABSTRACT: Detailed surface pressure measurements have been performed in the dilute regime for Langmuir monolayers of atactic poly(methyl methacrylate) chains spread at the air–water interface. Marked deviations from the ideal gas law give clear evidence for attractive interactions between the two-dimensional polymer chains. The second virial coefficient is negative and scales with the chain molecular weight as $A_{22}{}^{\Gamma} \propto M^{2\nu}$ when the concentration is measured in units of the number of chains $\Gamma = c/M$. For chains with molecular weights between 3250 and 18600, we obtain $\nu = 0.57 \pm 0.03$ for the Flory exponent describing the single-chain conformation $R_G \propto N^{\nu}$. This new, and independent, derivation of the ν exponent in two dimensions is in complete agreement with the value based on the concentration dependence of the surface pressure in the semidilute regime. This is the first time that the molecular weight dependence of the second virial coefficient is clearly established for polymer chains in two dimensions.

The interactions between flexible chains in dilute polymer solutions of finite concentration are generally described by the so-called virial coefficients. Numerous theoretical expressions have been proposed for the second-order virial coefficient A_2, which describes the average interactions between two polymeric chains. A pioneering approach by Yamakawa[1] describes all the dilute solution properties in terms of combinations of three parameters: the unperturbed dimension of the chain, the two-body excluded volume, and finally the three-body interactions between chain segments. His calculations are performed to first order with respect to the binary and ternary interactions. On the other hand, since a very long polymer chain is also a critical object,[2] the renormalization techniques developed in field theory are also applicable. Different schemes have been used. For example, Freed and his co-workers[3] have selected the cut-off regularization and the dimensional regularization to extend the perturbation calculations to values of the ternary interactions that were previously unaccessible. Their two separate approaches give an accurate treatment of the second and third virial coefficients for linear and branched polymers. Their expressions for A_2 and A_3 include important prefactors and apply to all dimensionalities, d, higher than 2. Similar calculations, but limited to $d = 4$, have been performed by Kosmas and Kosmas.[4] Witten and Schäfer[5] and des Cloizeaux,[6,7] working independently, have used direct renormalization, which makes no reference to the analogy between polymer chains and magnetic systems. They have performed $\epsilon = 4 - d$ expansions to calculate A_2 to first[5,6] and second[7] order in ϵ. Since these authors were mainly considering swollen chains in goods solvents, only binary interactions were taken into account. Some years earlier, Daoud and Jannink[8] had taken a simpler approach, based on the magnetic analogy, and used scaling arguments to derive the asymptotic dependence of A_2 on temperature and molecular weight. Their results are therefore only valid in the limit of infinite molecular weight samples. This first-step approach is interesting, however, in so far it allows us to make predictions in the entire temperature–concentration phase diagram of the polymer solution and can readily be tested experimentally. Moreover, the values of the power law exponents are not system dependent and should be solely defined once the space dimensionality and the universality class are specified. When polymer concentration is expressed as the number of chains per unit volume, Γ, the predicted scaling law is $A_2{}^{\Gamma} \propto N^{\nu d}$, where ν is the well-known Flory exponent and N is the chain degree of polymerization. When the polymer concentration is expressed in units of mass per unit volume, $c = M\Gamma$, where M is the chain molecular weight,

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