well-characterized, and representative polymer sample can be used to calculate the power-law constants, C and ν, in the relationship $D = CM^{-\nu}$, where D is the infinite dilution z-averaged diffusion coefficient of the polymer sample.

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Polymer Molecular Weight Determination Using Liquid Crystals

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ABSTRACT: The thermodynamic treatment of the freezing-point depression is applied to the solute-induced depression of the nematic–isotropic transition temperature for a liquid-crystal solvent. It is shown that it should be possible to determine solute molecular weights up to $\sim 10^6$. The method is applied to samples of two polymers, polystyrenes and poly(ethylene oxides), dissolved in two different liquid crystals, N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) and p-azoxyanisole (PAA). Molecular weights up to 10^5 are determined with an accuracy of $\sim 20\%$.

It has recently been shown[2] that the two polymers, polystyrene and poly(ethylene oxide), are soluble in the nematic and isotropic phases of the liquid crystal N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA). We show here that an accurate molecular weight determination of the polymer in a thermotropic liquid-crystal solvent is possible, using the polymer-induced depression of the nematic–isotropic transition temperature. At least in principle, the determination should remain accurate to molecular weights of $\sim 10^6$, whereas the usual cryoscopic technique cannot be used beyond $\sim 3 \times 10^4$.

In a nematic liquid crystal, the rodlike molecules are aligned with their long axes parallel. At the nematic–isotropic transition, this long-range order is completely destroyed. This is a first-order transition, and it can therefore be subjected to a thermodynamic treatment analogous to that of the melting of a crystal. The effect of a polymeric solute in the nematic phase of a liquid-crystal solvent is a decrease of the nematic order, and hence the nematic–isotropic transition temperature will be lowered. The transition is not sharp, as in the pure liquid crystal, but occurs over a temperature range where the nematic and isotropic phases are in equilibrium. This is illustrated in the schematic phase diagram in Figure 1. Here the lower $(T,w_2)^{\mathrm{N}}$ boundary indicates were the isotropic phase first appears on heating, while the upper $(T,w_2)^{\mathrm{I}}$ boundary indicates where the nematic phase first appears on cooling. The two-phase boundaries meet at the single nematic–isotropic transition temperature of the pure solvent, T_1^0. The shape of the two-phase boundaries has been discussed elsewhere.[2,3]

Cryoscopic and Liquid-Crystal Determinations of Molecular Weights. The cryoscopic determination of solute molecular weight is based on the freezing-point depression as given by the familiar van't Hoff equation:[4]

$$\Delta T = \frac{R(T_1^0)^2}{1000\Delta h_1^0} m_2 = K m_2 \qquad (1)$$

Here K is the molal freezing-point constant (in units of deg mol^{-1}) and m_2 is the molal concentration of the solute. The pure solvent freezes at T_1^0 with a latent heat of fusion, Δh_1^0, expressed per gram. Rearranging the equation to yield the unknown molecular weight gives

$$M_2 = \frac{R(T_1^0)^2}{\Delta h_1^0} \frac{w_2}{\Delta T} \qquad (2)$$

where w_2 is the weight fraction of the solute in the liquid solution.

Rothmund[5] has extended the van't Hoff freezing-point equation to include the case where the solute forms a mixed crystal with the solvent. The solute molecular weight is now obtained through

$$M_2 = \frac{R(T_1^0)^2}{\Delta h_1^0 \Delta T}(w_2^{\mathrm{liquid}} - w_2^{\mathrm{crystal}}) \qquad (3)$$

which reverts to the van't Hoff equation if $w_2^{\mathrm{crystal}} = 0$.

A detailed thermodynamic treatment of liquid-crystal + solute-phase diagrams has previously been given,[2,3] and the results show that there is a complete analogy between the depression of the nematic–isotropic transition tem-

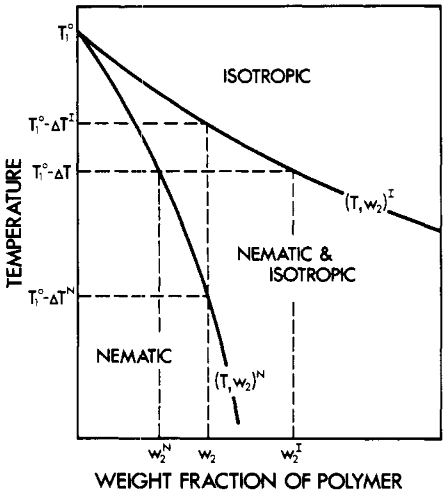

Figure 1. Schematic phase diagram of a liquid crystal + polymer system. The $(T,w_2)^I$ boundary is where the nematic phase first appears on cooling, and the $(T,w_2)^N$ boundary is where the isotropic phase first appears on heating. The horizontal line at $(T_1^0 - \Delta T)$ refers to eq 4, and the vertical line at w_2 refers to eq 6.

perature and the freezing-point depression, both of these transitions being first order. The Rothmund equation is valid with the nematic and isotropic phases taking the place of the crystal and liquid phases,

$$M_2 = \frac{R(T_1^0)^2}{\Delta h_1^0 \Delta T}(w_2^I - w_2^N) \qquad (4)$$

with T_1^0 the transition temperature of the pure liquid crystal, Δh_1^0 the enthalpy of the transition per gram, ΔT the temperature interval below T_1^0, and w_2^N and w_2^I the solute weight fractions in the nematic and isotropic phases in equilibrium.

Experimentally, one makes a sample, with concentration w_2, and determines the temperatures at which the isotropic phase starts to appear on heating ($T_1^0 - \Delta T^N$) (see Figure 1) and the temperature at which the nematic phase starts to appear on cooling, i.e., $T_1^0 - \Delta T^I$. A geometric consideration of Figure 1 gives at low solute concentration,

$$\frac{w_2^N}{\Delta T} \simeq \frac{w_2}{\Delta T^N};\ \frac{w_2^I}{\Delta T} \simeq \frac{w_2}{\Delta T^I} \qquad (5)$$

Equation 4 can therefore be changed to a more useful form,

$$M_2 = \left[\frac{R(T_1^0)^2}{\Delta h_1^0}\right] w_2 \left(\frac{1}{\Delta T^I} - \frac{1}{\Delta T^N}\right) \qquad (6)$$

Since the freezing-point depression is a colligative property, the molecular weight, obtained through eq 6, will be a number average molecular weight.

The efficiency of the cryoscopic and liquid-crystal determinations of M_2 depends on having a small value of Δh_1^0 for the transition or a large value of K in eq 1. Typical values are found in Table I where the globular molecules, cyclohexanol and camphor, which form plastic crystals are seen to be exceptionally good solvents for the cryoscopic determination of M_2. Liquid crystals, however, show even larger values of K because of their small heats of transition when going from the nematic to the isotropic phase. Thus, polymer molecular weights from 20 to a 100 times larger can be determined by using a liquid crystal as a solvent. Using solvents like benzene, the cryoscopic method measures molecular weights up to ~30 000, and hence molecular weights up to ~10^6 could be determined from the nematic–isotropic temperature depression. If the polymer concentration in EBBA is 1% (by weight), this would correspond to a ΔT of 0.005 °C, which is measurable. Resolutions of 10^{-4} degrees have been reported in several cases.[6] In the present work, each temperature measurement was to within ±0.02 °C, and thus the total ΔT was to within ±0.04 °C, which puts an upper limit of ~10^5 on the polymer molecular weight which could be measured.

Table I
Heats of Transition and Transition-Depression Constants

solvent	heat of transition (Δh_1^0), J g^{-1}	K, deg m^{-1}
cryoscopic		
water	333	1.86
benzene	127	5.09
cyclohexanol	19.6	37.7
camphor	42.3	39.6
liquid crystal		
EBBA	1.9[a]	5.5 × 10^2
PAA	2.8[b]	4.9 × 10^2
MBBA	1.06[c]	8.1 × 10^2

[a] G. W. Smith and Z. G. Garlund, *J. Chem. Phys.*, 59, 3214 (1973). [b] E. M. Barrell, R. S. Porter, and J. F. Johnson, *J. Phys. Chem.*, 68, 2810 (1964). [c] T. Shinoda, Y. Maeda, and H. Enokido, *J. Chem. Thermodyn.*, 6, 921 (1974).

Experimental Section

Two liquid crystals were used as solvents. They are N-(p-ethoxybenzylidene)-p-n-butylaniline (EBBA) and p-azoxyanisole (PAA). The experimental data of the EBBA + polymer systems, shown in Table II, have been extracted from phase diagrams published previously.[2] The polymers, listed in Table II, are polystyrene (PS), poly(ethylene oxide) with two hydroxyl end groups (PEO), and poly(ethylene oxide) with both end groups methylated (DMPEO). The nominal molecular weights listed in column 1 of Table I are given by the manufacturer. For all the polystyrenes, $M_n/M_w \leq 1.1$. More details of the materials and methods for the EBBA + polymer systems are given in ref 2. The PAA was obtained from Sigma Chemical Co., Saint Louis, Mo., and was used without purification. The nematic–isotropic transition temperature, T_1^0, was determined to be 407.4 K (the corresponding temperature for EBBA varies between 350 and 353 K, depending on the purity).

The experimental procedure was as follows. One first obtains ΔT^I for the polymer sample. This is simply determined visually by slowly (0.1 °C/min) cooling a sample that is completely isotropic. When the nematic phase first appears, the whole sample goes completely turbid, and later the two phases, nematic and isotropic, separate. The measurement would take typically ~15 min. If $M_2^I >$ ~10^4, no measurement of ΔT^N need be undertaken, according to eq 6, since $\Delta T^N \rightarrow \infty$. However, if $M_2^I < 10^4$, ΔT^N is determined by leaving the sample at different preset temperatures and noting the temperature at which a minute amount of isotropic liquid is in equilibrium with the nematic phase. The speed of separation of the isotropic phase from the nematic phase is dependent on the density difference between the two phases. Hence the length of time of the measurement might vary considerably, but typically is ~2 h. The heat of transition data used in eq 6 are shown in Table I.

It is important to realize that since the transition point depression is a colligative property, the polymer sample must be free from low molecular weight impurities, such as moisture. If the liquid-crystal solvent has a small molecular weight impurity, such as one of the starting materials for its synthesis, a two-phase region will be found for the "pure" solvent, which in our samples was so small that its T_N and T_I could not be distinguished. However, there seem to be no very stringent purity requirements on the liquid-crystal solvent. In the present work, EBBA samples were used having, as indicated above, a wide range of purities. Except in two cases to be discussed below, the molecular weight data reported in Table II are reasonable. Furthermore, phase-diagram data obtained by different workers[7] using MBBA of different purities are also in reasonable agreement for several solutes. This experience suggests that the purity of the liquid

Table II
Phase-Diagram Data for Polymers in EBBA and PAA and Experimental M_2

	ΔT^{I}, deg (at $w_2 = 0.01$)	ΔT^{N}, deg (at $w_2 = 0.01$)	M_2^{I}, g mol^{-1}	M_2, g mol^{-1}
EBBA				
PS (600)	2.9	4.2	1.9×10^3	0.6×10^3
PS (2100)	1.6	4.7	3.5×10^3	2.3×10^3
PS (4000)	0.9	4.1	6×10^3	5×10^3
PS (20400)	0.3	∞	2×10^4	2×10^4
PEO (1540)	1.8	6.0	3.1×10^3	2.2×10^3
PEO (4000)	0.4	∞	14×10^3	14×10^3
DMPEO (2000)	1.6	4.4	3.5×10^3	2.2×10^3
DMPEO (6000)	0.2	∞	3×10^4	3×10^4
PAA				
PS (20400)	0.2	∞	2×10^4	2×10^4
PS (110000)[a]	0.05	∞	1×10^5	1×10^5
	0.07	∞	1×10^5	1×10^5
	0.14	∞	1.2×10^5	1.2×10^5
DMPEO (6000)	0.7	2.0	7×10^3	5×10^3

[a] Obtained at a polymer weight fraction different from 0.01.

crystal is not of critical importance. This may seem less surprising if it is realized that one measures the *changes* ΔT^{I} and ΔT^{N}, on addition of the polymeric solute, relative to the experimental transition temperature of the particular liquid-crystal sample (or if they are separable, the T^{I} and T^{N} of the sample). We have shown using eq 1–6 that this procedure should lead to the correct M_2 in the special case that neither the polymer nor the impurity enters the nematic phase. Experiment seems to show that the procedure is generally valid.

Results and Discussion

Table II gives the temperatures ΔT^{I} and ΔT^{N} for a weight fraction of 0.01 of polymer, and in the last column the value of M_2 determined using eq 6 is given. Apart from two cases to be discussed below, the values are within ~20% of the nominal M_2.

It is easily realized from eq 4 that the concentration interval of the nematic–isotropic two-phase region is directly proportional to the solute molecular weight. This implies that, as the solute molecular weight increases, the $(T,w_2)^{\mathrm{N}}$ boundary will approach the temperature axis in the phase diagram of Figure 1. In other words, the solute will become less soluble in the nematic phase as its molecular weight is increased, i.e., $w_2^{\mathrm{N}} \rightarrow 0$ or $\Delta T^{\mathrm{N}} \rightarrow \infty$, so that the second term in eq 6 decreases in importance. We also note that, as the solute molecular weight increases, the slope of the $(T,w_2)^{\mathrm{I}}$ boundary, or ΔT^{I}, will decrease, i.e., the first term in eq 6 will increase in importance. For a comparison, we have, in Table II, listed both M_2^{I}, which is the solute molecular weight obtained from eq 6 when omitting the last term, and M_2, which is obtained from eq 6, taking both terms into consideration. We conclude from the table that it is important to determine ΔT^{N} only for the lower molecular weight solutes, in this case when $M_2 \leq 10^4$.

Experiments were also made with solutes of very low molecular weight, viz., ethylbenzene and ethylene oxide oligomers of $M_2 \approx 200$–300. The experimental M_2 were too large by factors of ~3. As seen in the schematic phase diagram in Figure 1, the $(T,w_2)^{\mathrm{I}}$ boundary is curving upwards while the $(T,w_2)^{\mathrm{N}}$ boundary has a downward curvature. This implies that the determined solute molecular weight, which is proportional to the width of the two-phase region, will be larger than its real value, since one necessarily has to determine the phase boundaries at some finite solute concentration. We believe it is this effect which accounts for the incorrect values when the molecular weight is ~200–300. Only at infinite solute dilution will the determined molecular weight be identical with its real value. A correction procedure, which allows extrapolation to infinite solute dilution, has been outlined,[3] but unfortunately it requires the solute molecular weight as a parameter and can therefore not be used in our case. To make the best out of the case, one should therefore work at the lowest possible solute concentration.

In Table II, the experimental M_2 are much too large in the EBBA + PEO (4000) and EBBA + DMPEO (6000) systems. Two explanations have been given.[2] First, it is known[8] that PEO chains associate in certain organic solvents, and the higher molecular weights found here could well be due to this phenomenon. Second, however, there is evidence[9] that higher molecular weight PEO may exist in either a partially helical or a random-coil conformation depending on the solvent. It is thus not excluded that the incorrect molecular weights could be due to a different conformation for the PEO in the nematic and isotropic phases, helical in the former and random coil in the latter. Both of these possibilities are discussed in more detail in ref 2. Note that there is no anomaly in the PAA + PEO (6000) system. This would indicate that the aggregates or helices are broken up at the higher temperature of the PAA systems (~134 °C compared with ~80 °C for the EBBA systems).

The results in the case of the PS (110 000) must be considered very approximate since the value of ΔT^{I} is of the same order as the accuracy of ΔT^{I} itself. EBBA was also used for the determination of the molecular weight in this case and gave a value which was too small by a factor of 2. This, however, might have resulted from a liquid–liquid separation.

Our general conclusion is that the method is promising enough to merit further study. Perhaps most important, it is convenient, particularly for high molecular weights where only ΔT^{I} need be measured through simply cooling the solution and observing the onset of turbidity.

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Electron Diffraction Investigation of a High-Temperature Form of Poly(vinylidene fluoride)

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ABSTRACT: Thin films of poly(vinylidene fluoride), crystallized from the melt at temperatures above 160 °C, were examined by electron microscopy and diffraction. Immature spherulites of a high-melting form were found to be composed of collections of flat platelets with remarkably regular crystallographic growth facets. Electron diffraction patterns from these are not consistent with any of the commonly accepted unit cells for this polymer but are instead in agreement with a new unit cell that has recently been found in solution-grown samples and appears to be the correct one for γ-PVF$_2$. When tilted in the electron microscope, these melt-crystallized samples yielded diffraction patterns indicating that the molecular chains are not normal to the broad lamellar surfaces but are instead rotated about the *b* axis of the unit cell to an angle of 28.5° from the lamellar normal.

Poly(vinylidene fluoride) [PVF$_2$] is commonly obtained in two crystallographic modifications. The α form is the one predominantly observed during crystallization from the melt[1,2] and has been characterized by a large number of investigators.[3-13] Gal'perin et al.,[3,4] Natta and coworkers,[5] Doll and Lando,[6] and Hasegawa et al.[13] have analyzed its structure by X-ray diffraction; infrared spectroscopy has been employed by Cortili and Zerbi[8] and Enomoto et al.,[9] while Boerio and Koenig[10,11] have used Raman scattering. Farmer and co-workers[7] and Hasegawa et al.[12] have also applied potential energy calculations to the crystallographic study of α-PVF$_2$. Although minor differences in interpretation exist among these workers, the consensus has been that the α form consists of molecular chains adopting conformation II (essentially a slight variant of a $TGT\bar{G}$ conformation). On the basis of the latest crystallographic data,[13] the unit cell of α-PVF$_2$ is monoclinic (pseudo-orthorhombic), with a = 4.96 Å, b = 9.64 Å, c(chain axis) = 4.62 Å, and β = 90°, and contains two molecular chains.

The second major polymorph of PVF$_2$ is the β form, usually obtained by mechanical deformation of α spherulites. Its structure has been investigated by the above authors[3-5,7-9,12,13] and by others.[14-16] The molecular chains in β-PVF$_2$ adopt conformation I, which is either a fully planar zigzag[7,14] or a slight variant thereof, as suggested by Gal'perin and co-workers[3] and Hasegawa et al.[12,13] The latter authors found that to relieve the strain from adjacent fluorine atoms in an all-trans conformation, statistical deflections of CF$_2$ groups at an angle of 7° about the plane of the zigzag yield optimum experimental agreement both with X-ray intensities[13] and potential-energy calculations.[12] The unit cell of β-PVF$_2$ is orthorhombic and contains two molecules in a C-centered arrangement; its dimensions are a = 8.58° Å, b = 4.91 Å, and c(chain axis) = 2.56 Å.

In addition to these, two other polymorphs have been described in the literature. The γ form has been reported to grow from solution in dimethyl sulfoxide, dimethyl acetamide, and dimethyl formamide,[17,18] as well as from the melt at high pressures[19-21] and high temperatures.[1,2] On the basis of work by Hasegawa et al.,[13] its unit cell has for years been considered as only slightly different from that of β-PVF$_2$: the same number of molecular chains in the same conformation is thought to pack monoclinically with a = 8.66 Å, b = 4.93 Å, c(chain axis) = 2.58 Å, and β = 97°. However, an alternative γ-unit cell (discussed in detail later in this paper) has very recently been proposed by Weinhold et al.[22] The last known polymorph of PVF$_2$ has been reported[23,24] to be a polar version of the α form, obtained by rotation of alternate molecular chains under the influence of high electric fields.

As has been mentioned above, evidence for the crystal structures of the various polymorphs of PVF$_2$ has come almost exclusively from infrared and X-ray diffraction studies. Electron diffraction, whose ability to yield single crystal-like patterns from appropriate samples renders it particularly useful in structure determination, has only sporadically been applied to this polymer.[16,25-27] It is for this reason that we have undertaken a detailed electron microscopic study of melt-crystallized PVF$_2$. This paper consists of an analysis of electron diffraction data from certain crystalline regions whose structure could not be reconciled with any of the commonly accepted unit cells[13] for PVF$_2$; the morphological aspects of this investigation are described separately.[28]

Experimental Section

The PVF$_2$ samples studied were Kynar 821, obtained from Pennwalt Corp. Molecular weight averages, calibrated in terms of polystyrene fractions, were $\bar{M}_w$ = 541 000 and $\bar{M}_n$ = 337 000. Thin films of this polymer, suitable for electron microscopy, were deposited on freshly cleaved mica from dilute solution in dimethylformamide. The films were then melted and held at 200–220 °C for up to 30 min prior to recrystallization at the desired temperatures (ranging from 160 to 165 °C) in a Mettler FP5 microscope hot stage. After 24 h at 162 °C, gel permeation chromatography yielded $\bar{M}_w$ = 511 000 and $\bar{M}_n$ = 310 000, indicating that degradation had not occurred to any significant extent. Samples for electron microscopy were shadowed using

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