COMPARATIVE STUDIES OF THE SOLUTION PROPERTIES OF

VINYL AROMATIC POLYMERS

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SYNOPSIS

Viscosity and NMR studies of poly-1-vinylnaphthalene, poly-2-vinylnaphthalene, and polyvinylbiphenyl solutions were carried out over a range of temperatures. Two transition temperatures, 20°C and 50°C, are found. The analysis of $[\eta]$-T-M relations yields the short and long range interaction parameters as a function of temperature. The conformational parameter $\sigma = (<r_\theta^2>/<r_{of}^2>)^{1/2}$ and the temperature coefficient $(d\ln<r_\theta^2>/dT)$ have been evaluated. From the NMR studies of P2VN-68 solutions the activation energy of the main transition at 50° is calculated as $E = 23 \pm 4$ kcal/mol for 100% polymer, indicating strong hindrance of motions. The transition has been ascribed to motions of the backbone chain.

INTRODUCTION

Investigations of the solution properties of vinyl aromatic polymers
(PVAr) such as poly-1-vinylnaphthalene[1] (P1VN), poly-2-vinylnaphthalene[1b,2]
(P2VN) and polyvinylbiphenyl[1b,3] (PVB) have been carried out by a number of
authors. In addition, the crystal structure of isotactic P1VN (identity period,
type of helix, angles of internal rotation and valence bonds) has been studied[4].
On the basis of the aforementioned studies, two conclusions have been reached:
a) the values of the parameter $\sigma \equiv (<r_\theta^2> /<r_{of}^2>)_{N=const.}^{1/2}$ (where $<r_\theta^2>$ and $<r_{of}^2>$
are unperturbed and freely rotating model mean square end-to-end distances re-
spectively, and N is the number of statistical segments) are similar[3a] for
PVAr ($\sigma \approx 2.3$) and for polystyrene (PS); and b) P2VN undergoes a reconfigurational
change at a temperature t_2 with $45 \leq t_2 \, °C \leq 70$, depending on the method of measure-
ment[2c].

A detailed study of the temperature dependence of the conformation and
configuration of PVAr molecules in solution is desirable and three independent
series of measurements were carried out, namely intrinsic viscosity determinations
on a number of samples of each polymer in a temperature range from 20° to 75°C,
viscosity measurements of dilute solutions of each polymer in a sealed viscometer
between 5 and 75°C, and NMR spectroscopy of P2VN solutions at temperatures rang-
ing from ∿10°C up to ∿80°C. For the viscosity studies benzene solutions of PVAr
were used. High resolution NMR spectra were obtained in CCl_4 + dioxane.

EXPERIMENTAL

The polymer samples were prepared for the Jet Propulsion Laboratory[16] by
Dr. J. Heller at The Stanford Research Institute by anionic polymerization.

They were fractionated and characterized by gel permeation chromatography (GPC) calibrated independently for the M_n and M_w of each polymer. Later the samples were reprecipitated in our laboratory by the slow introduction of the benzene solution of PVAr to a large volume of MeOH, filtered and dried in a vacuum oven for two weeks at 50°C. Selected samples of these polymers measured before and after reprecipitation showed no change in $[\eta]$ and the Huggins parameter k_1 . In addition vacuum sealed ampules of the polymers were kept for two weeks in an oil thermostat at 75°C in the dark. The solutions of such thermally treated samples of P1VN and P2VN contained a few white flocks of insoluble material. The change in viscosity properties of the solutions was found to be small. For example, the $[\eta]$ and k_1 of P2VN-44 at 20°C in benzene are as follows:

before the thermal treatment $[\eta]$ = 1.056, k_1 = 0.37

after 2 weeks at 75°C, without filtration $[\eta]$ = 1.058, k_1 = 0.36

after 2 weeks at 75°C, with filtration $[\eta]$ = 1.050, k_1 = 0.36.

The results for P1VN were similar. No changes for PVB were noted.

A further check on the polymers' thermal stability was made in their benzene solutions. Keeping the solutions one hour at 70°C, under normal measurement conditions (air, daylight) did not cause any significant changes in $[\eta]$ and/or k_1.

On the basis of this evidence we conclude that the polymers are stable under the experimental conditions within the limit of experimental error. The characteristics of all samples are presented in Table I.

Analytical, reagent grade, thiophene-free benzene was further purified by rectification on a packed column over sodium wire. For all the viscosity experiments a middle fraction (B.P. = 80.0-80.1°C) from the same batch was used. Spectrum grade CCl_4 and dioxane were used for NMR determinations.

TABLE I.

CHARACTERISTICS OF PVAr AND PS SAMPLES

SYMBOL	$M_w \cdot 10^{-3}$ GPC	LSc	M_w/M_n GPC	LSc/Osm	$T_g \pm 1°C$	$-(\partial \ln [\eta]/\partial T)_M \cdot 10^3$
P1VN-59	155.3	167	1.14	1.43	159	1.1
P1VN-66	147.3	154	1.48	1.77	---	1.2
P1VN-88	103.4	96	1.05	1.15	---	1.3
P1VN-8036	52.2	44	1.06	1.52	---	1.7
P2VN-44	736.1	676	1.55	1.38	151	2.1 (t<t₂), 0.5 (t>t₂)
P2VN-70	563.4	500	1.88	1.48	---	2.1 (t<t₂), 0.7 (t>t₂)
P2VN-58	306.1	346	1.41	1.37	---	1.9 (t<t₂), 0.4 (t>t₂)
P2VN-48	182.5	202	1.29	1.56	---	2.0 (t<t₂), 0.2 (t>t₂)
P2VN-68	64.0	64	---	1.05	---	2.2 (t<t₂), 0.3 (t>t₂)
P2VN-61	48.9	57	---	---	147	2.0 (t<t₂), 0.3 (t>t₂)
PVB-63	1104.	1670	2.15	3.25	161	1.61
PVB-41	706.5	735	2.06	1.60	---	1.11
PVB-71	169.4	190	1.45	1.33	---	0.71
PVB-56	103.0	94	1.52	1.51	---	0.10
PVB-51	80.8	74	1.26	1.14	---	0.044
PVB-8036	10.5	---	---	---	---	-0.044

For the intrinsic viscosity determinations the polymer solutions were prepared in volumetric flasks one day before use. The polymer-solvent mixture was heated up to 50°C for half an hour. Concentrations were calculated from the weights and densities of the components. Due to special care during the purification, the polymers and solvents were dust free, and the solutions did not require filtration.

The [η] measurements were carried out in a Hewlett-Packard auto-viscometer model 5901B with a constant temperature bath model 5910A using Cannon Ubbelohde dilution viscometers, calibrated by means of NBS standard viscosity oils. For the temperature coefficient of solution viscosity a specially designed viscometer (Fig.1) was used. After many degassing cycles on the high vacuum line the apparatus was sealed off, placed on a wheel-like mount and immersed into a thermostatic bath. The mount allowed the viscometer to be rotated in order to refill it after each run. The instrument has been calibrated for the kinetic energy correction in the whole temperature range, using high purity organic solvents. Usually two series of measurements on each solution were carried out from 75°C down to 5°C and from 5°C up to 75°C within a two day period. The results were superimposable. For the calculations the smoothed values of solvent viscosity were used. In order to avoid a pressure correction for the viscosity, measurements were carried out in the temperature range of 5°C-75°C, where the vapor pressure of benzene varies from 40-640 mm Hg.

For both series of measurements, in the Cannon Ubbelohde and in the sealed viscometer, the kinetic and density corrections were applied either by using the previously derived equations[5] or converting each efflux time into viscosity.

The NMR spectra were determined by Mr. S. Surface through the courtesy of Dr. K. L. Servis of this University on a Varian HA-100 equipped with a V-4311

100 Mc fixed frequency RF unit, a V-4014 23,490 gauss magnet and a V-4341 variable temperature control unit. The exact temperature of the setting was determined after each run from the chemical shifts of MeOH.

A Perkin-Elmer Differential Scanning Calorimeter, Model 1B, was used to check the thermospectra of PVAr in a temperature range from 0°C to 230°C. The glass transition temperature T_g was easily detectable, but we were unable to see any other transition in this range of temperatures. The T_g data, extrapolated to zero scanning rate, are shown in Table I.

It is worth mentioning that the P2VN solutions of the two lowest molecular weight samples at room temperature showed some inherent turbidity, which increased with concentration and decreased with temperature. Under the same conditions P1VN solutions were completely transparent. Samples of these polymers cast in three weeks from benzene solution were observed under a polarization microscope and by X-ray diffraction analysis. For the latter a Norelco powder camera was used. Samples were exposed for 12 hours to copper $K\alpha$ radiation. The X-ray diagram of P2VN shows a diffraction pattern corresponding to a distance $d_1 = 1.94$ Å . P1VN exhibits two distinct diffraction lines, from which the spacings $d_1 = 1.95$Å and $d_2 = 4.1$ Å were determined. Due to the strong amorphous band it was impossible to establish any higher d_n.

From the depolarization of light and diffraction pattern, both of which are observed only for P1VN, we conclude that the polymer is partially crystalline. The spacings d_1 and d_2 are close to those calculated from unit cell dimensions[4]. The same spacing in P2VN may indicate partial regularity.

RESULTS

The intrinsic viscosities between 20°C and 75°C are shown in Table II and in Figs. 2-4. In Table II the k_1-values are also listed. From these data the temperature coefficients $D = (\partial \ln[\eta]/\partial T)_M$ are calculated, see Table I. Especially noteworthy is the sharp change of D for P2VN at $t_2 = 46°C$, in contrast to the two other PVAr-solvent systems.

In Fig. 5 we present viscosities for fixed c and M as a function of temperature for PVAr and PS, as determined in a sealed viscometer. The same two transition temperatures exist for all four polymers, namely $t_1 \overset{\sim}{=} 20°C$ and $t_2 \overset{\sim}{=} 50°C$. In Table IV activation energies of flow

$$\Delta H^{\pm}/R = (\partial \ln \eta_{sp}/\partial(1/T))_{M,c}$$

calculated for the three ranges of temperature are shown.

The NMR studies were conducted on three solutions of P2VN-68, using as solvent mixtures of dioxane in CCl_4 in a ratio of 1:10 by volume. The polymer concentrations are 7.6 , 11.8 and 18.3 wt. %. As expected, at higher temperatures better resolution was obtained using more concentrated solutions. However at lower temperatures the dilute solutions yielded better defined spectra. In all cases three peaks with positions at 30° at 1.75τ, 1.75τ and 7.44τ were observed. These may be assigned respectively to hydrogens of aromatic R-groups, the α-hydrogen in $=CHR$ and β-hydrogens in $=CH_2$. We find that from 22°C up to 80°C the positions of the 1.75 and 7.14 peaks remain constant, whereas the third peak shifts from 7.41τ up to 7.61τ. In the text however, we will use its position at 30°C, i.e., 7.44τ to designate this peak.

TABLE II.

INTRINSIC VISCOSITY [n] AND HUGGINS PARAMETER k_1 OF PVAr AS A FUNCTION OF TEMPERATURE t.

SAMPLE	t = 20 [n]	t = 20 k_1	t = 30 [n]	t = 30 k_1	t = 45 [n]	t = 45 k_1	t = 65 [n]	t = 65 k_1	t = 75 [n]	t = 75 k_1
P1VN-59	0.383	0.44	0.379	0.44	0.375	0.45	0.368	0.43	0.361	0.48
P1VN-66	0.367	0.38	0.364	0.41	0.358	0.41	0.349	0.44	0.342	0.50
P1VN-88	0.271	0.45	0.268	0.48	0.264	0.57	0.254	0.46	0.248	0.60
P1VN-8036	0.155	0.46	0.151	0.47	0.148	0.61	0.142	0.75	0.140	0.78
P2VN-44	1.073	0.36	1.059	0.36	1.025	0.39	1.011	0.39	1.001	0.39
P2VN-70	0.886	0.36	0.864	0.38	0.842	0.40	0.827	0.40	0.808	0.45
P2VN-58	0.667	0.34	0.656	0.41	0.633	0.39	0.634	0.32	0.626	0.35
P2VN-48	0.456	0.41	0.446	0.43	0.433	0.45	0.434	0.39	0.430	0.34
P2VN-68	0.211	0.47	0.207	0.49	0.201	0.57	0.198	0.43	0.193	0.44
P2VN-61	0.180	0.50	0.177	0.50	0.170	0.58	0.168	0.51	0.165	0.48
PVB-63	1.342	0.33	1.326	0.36	1.289	0.37	1.262	0.35	1.215	0.36
PVB-41	0.927	0.35	0.917	0.34	0.914^{50}	0.36^{50}	0.908	0.36	0.897	0.35
PVB-71	0.375	0.56	0.370	0.53	0.369	0.55	0.363	0.50	0.360	0.43
PVB-56	0.243	0.48	0.242^{25}	0.53^{25}	0.239	0.52	0.237	0.53	-----	-----
PVB-51	0.217	0.48	0.214^{35}	0.48^{35}	0.213	0.56	0.212	0.39	0.210	0.42
PVB-8036	0.069	0.55	0.070	0.56	-----	-----	0.070	0.51	-----	-----

Note: Superscripts indicate temperature other than that of the column heading.

TABLE III.

PARAMETERS K AND a, OF eq. (1) FOR PVAr

IN BENZENE AND FOR ATACTIC PS (θ)

POLYMER	t°C	a	$K \cdot 10^4$	Ref.
P1VN	20	0.82	0.220	this work
P1VN	75	0.88	0.103	"
P2VN	20	0.719	0.690	"
P2VN	75	0.695	0.869	"
P2VN	20	0.71	0.66	2b
PVB	20	0.619	2.140	this work
PVB	75	0.589	2.774	"
PVB	25	0.69	0.92	3
PS-atactic, (various solvents)	T=θ≈30	0.5	7.1-8.2	7

TABLE IV

TEMPERATURE COEFFICIENT OF SOLUTION VISCOSITY OF PVAr AND PS

CALCULATED FROM SEALED VISCOMETER DATA

POLYMER	CONCN. wt %	$-[\partial \ln \eta_{sp}/\partial(1/T)]_{c,M} \cdot 10^3$			$(\partial \ln k_1/\partial T)_M \cdot 10^3$	
		t<20	20<t<50	t>50	t<50	t>50
P1VN-59	2.73	244	115	0.00	0.29	6.60
P2VN-70	0.65	306	90	28	8.52	4.12
P2VN-61	6.04	409	225	56	0.17	-0.43
PVB-41	0.72	186	48	-20	2.04	5.09
PS ($M_h = 2.21 \times 10^5$)	1.05	253	103	32	----	----

2. Unperturbed dimensions of PVAr coils

It has been pointed out[8] that $\log K$ is a linear function of $(a-1/2)$ with the constants characteristic for a given polymer-solvent system. Hence, the unperturbed coil dimensions can be obtained by going to the limit $a \to 1/2$, viz:

$$\lim_{a \to 1/2} K = K_\theta \tag{2}$$

The limitation of this procedure lies in the fact that it does not yield the θ-temperature itself.

The parameter defined as $K_\theta = [\eta]_\theta / M^{1/2}$, can be expressed as

$$K_\theta = \Phi_\theta A^3 \tag{3}$$

where Φ_θ is a universal constant and the short range interaction parameter $A = (\langle r_\theta^2 \rangle / M)^{1/2}$. In this paper we will use the value $\Phi_\theta = 2.87 \times 10^{21}$. (For a more detailed discussion of this quantity see reference 9.)

Fig. 8 exhibits the K-a plots for three PVAr from Table III. A common straight line results with the intercept $K_\theta = (7.69 \pm 0.25) \times 10^{-4}$. It is interesting to note that literature values for PS[7] lie in the range $7.1 \leq K_\theta \times 10^4 \leq 8.2$.

From the above data the parameter σ for P1VN and P2VN is found to be $\sigma = 2.59 \pm 0.03$, $\sigma = 2.81 \pm 0.03$ for PVB and $\sigma = 1.99 \pm 0.02$ for PS. More precise information on the short and long interaction parameters can be obtained directly from $[\eta]$-M data. At the present time there exist a number of theoretical or semitheoretical equations derived for this purpose. Their applicability and reliability have often been discussed[10]. It is generally accepted that the simple Stockmayer-Fixman[11]

equation

$$[\eta]/M^{1/2} = K_\theta + 0.51 \phi_\theta B M^{1/2} \qquad (4)$$

of the type proposed earlier by W. Kuhn, where B is a long range interaction parameter, is applicable when the expansion coefficient α_η does not exceed 1.4 . The numerical values derived from eq. (4) vary within 2% of those from more elaborate equations[10a,12]. The analysis of $[\eta]$-data presented here is based on eq. (4).

At 30°C we find in this manner (see Fig. 9) $K_\theta \times 10^4$ = 2.42, 6.47 and 6.30 for P1VN, P2VN and PVB respectively with a standard derivation of ± 0.03 . Therefrom σ = 1.76, 2.45, 2.63 (±0.01). These values arise from the use of the GPC molecular weights which involve a smoothing of the column factor Q_w^{1b} . If on the other hand, the lightscattering data are employed directly, the result is: $K_\theta \times 10^4$ = 6.54, 6.13 and 6.40 ± (0.06); σ = 2.46, 2.41, 2.64 ± (0.01). However, the lowest molecular weight in P1VN and P2VN and the highest molecular weight in PVB are incompatible with the linear relationship (4). This is the case over the whole temperature range investigated and thus can not reflect errors in $[\eta]$. The above values were obtained by omitting these particular points. The discrepancies between the two sets of K_θ do not exceed 5% for P2VN and PVB. For P1VN the values are at complete variance. Table V shows this to be the case over the whole temperature range. The errors are magnified by the narrow range of molecular weights and the high value of B, see Fig. 10.

In Fig. 9 is indicated for comparison the common value of K_θ = (7.69 ± 0.25)×10^{-4} derived from eq. (2). This consistently higher value should result from the extremely low (hypothetical) temperature at which a = 0.5. The similarity between the numbers

TABLE V

CONFORMATIONAL PARAMETER σ for PVAr and PS

POLYMER	V_x (ml/mol)	σ from eq. (2)	σ from eq.(4) 20°C	30°C	45°C	65°C	75°C
P1VN	137	2.59 ± 0.03	(2.48 ± 0.01)*	(2.46 ± 0.01)	(2.44 ± 0.00)	(2.34 ± 0.00)	(2.39 ± 0.03)
			1.83 ± 0.00	1.76 ± 0.00	1.74 ± 0.00	1.63 ± 0.01	1.63 ± 0.01
P2VN	137	2.59 ± 0.03	(2.43 ± 0.02)	(2.41 ± 0.01)	(2.36 ± 0.02)	(2.36 ± 0.02)	(2.36 ± 0.02)
			2.47 ± 0.00	2.45 ± 0.00	2.42 ± 0.00	2.41 ± 0.04	2.40 ± 0.01
PVB	180	2.81 ± 0.03	(2.65 ± 0.01)	(2.64 ± 0.01)	(2.63 ± 0.01)	(2.63 ± 0.01)	(2.63 ± 0.01)
			2.62 ± 0.01	2.63 ± 0.01	2.63 ± 0.01	2.63 ± 0.02	2.65 ± 0.03
PS	90	1.99 ± 0.02	----------	2.20**	----------	----------	----------

* Parentheses refer to results obtained from M_w(LSc)

** t = 35°C, ref. 10b

for the three polymers and the actual magnitude suggest that the light scattering value for P1VN is more nearly correct.

The literature data on the unperturbed dimensions of PVAr are limited and contradictory. The value $\sigma = 2.28$ for P2VN at 30.2°C in decalin/toluene (θ-solvent) can be derived from K_θ as reported by Eskin and Korotkina[2a], who on the other hand calculate $\sigma = 3.2$ from $<r_\theta^2>$, determined by light scattering in the same mixed solvent. For the same polymer Tsvetkov et al[2b] obtain $\sigma = 2.6$ from [η] data in benzene at 20°C, using $\Phi = 2.1 \times 10^{21}$. A σ of 2.44 can be computed for PVB from the K_θ value at 30°C in 2-methoxyethanol/dimethoxyethane reported by Moacanin et al[3]. The value of 3.2 determined by light scattering contains a large error due to neglect of selective solvent absorption by the polymer and the correction for the difference of refractive indices of the solvents. The data of Tsvetkov et al[2b], with $\Phi_\theta = 2.87 \times 10^{21}$ yield $\sigma = 2.34$. In conclusion, the values of σ presented here are slightly higher than those calculated from the literature data: 2.45[2.41] vs. 2.28-2.34 for P2VN, and 2.63[2.64] vs. 2.44 for PVB. Their relative magnitude however is the same; PVB has larger coil dimensions than P2VN. Unfortunately the literature contains no results for P1VN. Similar values for P1VN and P2VN have been indicated.

3. Longe range interaction parameter

In Fig. 10 the quantity B is plotted vs. 1/T. No change of slope occurs around a temperature t_2. However, only for P1VN is the usual temperature dependence, viz. $B = B_o(1 - \theta/T)$, observed with $B_o = 2.2\ [7.1] \times 10^{-27}$ and $\theta = -136°C$ [-165], where the parentheses refer to the light scattering data. This may be compared with the results of Inagaki et al[13] for atactic PS in transdecalin in the

neighborhood of t = θ, where B_o lies between 5.42 and 3.73×10^{-27}. Moreover, the linear dependence on 1/T applies only in the vicinity of θ, with B_o decreasing with increasing T. Berry[14], on the other hand, finds B_o constant over 100°C. The θ-temperature calculated fore P1VN is well in the range of θ's determined fore PS in benzene (-100°C) and toluene (-150°C).

The two other polymers exhibit a temperature dependence of B opposite to that of P1VN. There are two possible explanations: the existence of a LCST, or association. In the first case an increase of T should increase the turbidity of P2VN solutions. In fact it decreases with increasing temperature. On the other hand, solute association would account for the decrease of the turbidity of P2VN solutions with temperature, the relatively small temperature coefficient of B, and the slow process of thermal equilibration of the solutions. No definite proof of this hypothesis can be given on the basis of the experimental results presented.

Having established A and B values for PVAr, we examine the maximum values of α_η occurring under our experimental conditions in order to check if the approximation (4) is applicable. From the definition of α_η and eqs. (2) and (4) we have

$$\alpha_\eta^3 = 1 + 0.51(B/A^3)M^{1/2} \tag{5}$$

and the maximum values of α_η for P1VN, P2VN and PVB are less than 1.54 [1.12], 1.24[1.22] and 1.23[1.28] respectively.

4. Temperature coefficients of $[\eta]$ and $\langle r_\theta^2 \rangle$

The configuration of a polymer coil in solution is determined by the short and long range interaction parameters. For a full description of the system their temperature dependence is required.

The temperature coefficient of $[\eta]$ defined as

$$D \equiv (\partial \ln[\eta]/\partial T)_M$$

can be obtained from Table II and Figs. 2-4. Numerical values are shown in Table I. As mentioned previously, two different temperature coefficients result for P2VN solutions, depending on the T-range. For the other PVAr a single value obtains.

From eqs. (3) the relationship between $[\eta]$, A and B may be written as

$$[\eta] = \Phi_\theta A^3 M^{1/2} \alpha_\eta^3 \qquad (6)$$

(The correction of the numerical constant in eq. (6) proposed by Iwama et al[9] for better agreement between B's calculated from $[\eta]$ and second virial coefficient data will not be used in this paper.) Differentiation of eq. (6) leads to the expression

$$D = (3/2)D_r + (1-\alpha_\eta^{-3}) [D_B-(3/2)D_r] \qquad (7)$$

where

$$D_B \equiv (\partial \ln B/\partial T)_M, \qquad\qquad D_r \equiv (\partial \ln A^2/\partial T)_M$$

Equations (5) and (7) suggest a plot of D vs. $M^{1/2}$ and extrapolation to $M \rightarrow 0$ with

$$D_r = (2/3) \lim_{M \rightarrow 0} D \qquad (7a)$$

The slopes of the full lines in Fig. 9 were calculated from eq. (7a), using the D-values shown in Table I. The D_r were also computed from the K_θ determined at T = const. according to eq. (4). This procedure produces the points shown in Fig. 9.

Referring first to the GPC results, agreement between the two methods of calculation is obtained to a varying degree. For P1VN the two temperature coefficients are reasonably close. For P2VN eq. (7a) applied above and below t_2 yields two straight lines in Fig. 9 which are in good accord with the K_θ values. We are not justified to derive two temperature coefficients from eq. (4), and the single value quoted in Table VI is actually seen to be intermediate between the two D_r's, eq. (7a). The temperature coefficient for PVB is small from both methods of computation.

The comparison is considerably less satisfactory on the basis of the light scattering molecular weights except for PVB.

Finally, we may compare PVAr and PS. Bianchi et al[15] obtain for atactic PS in θ-mixtures at 6.6 and 32.8°C $D_r = -(1.8 \pm 0.4) \times 10^{-3}$, whereas Orofino[16] finds $D_r = + 0.6 \times 10^{-3}$ in several θ-solvents, and Utracki and Simha[17] compute $D_r \simeq 0$ from [η] in cyclohexane at t = 34.4 ± δ°C. These differences may represent specific solvent effects.

It is noteworthy that the temperature coefficient for PVB is nearly zero or positive, whereas for P1VN and P2VN we observe only negative values. In terms of a simple trans-gauche model this implies a T→G transition with increasing temperature for the latter polymers.

TABLE VI

TEMPERATURE COEFFICIENT OF THE UMPERTURBED

DIMENSIONS OF PVAr

| POLYMER | $D_r \times 10^3$ (deg.$^{-1}$) | | |
| | eq. (4) | eq.(7a) | |
		t<50	t>50
P1VN	(-0.77 ± 0.01)*	(-1.36 ± 0.04)	
	-1.87 ± 0.01	-1.63 ± 0.04	
P2VN	(-0.40 ± 0.01)	(-1.30 ± 0.11)	-0.10 ± 0.12
	-0.83 ± 0.03	-1.36 ± 0.10	-0.13 ± 0.10
PVB	(-0.07 ± 0.00)	(0.16 ± 0.15)	
	0.23 ± 0.01	0.20 ± 0.16	

* Parentheses refer to results obtained from M_w(LSc)

We can proceed a little further by assuming P1VN to be partially isotactic. According to Natta[4] a stereoregular polymerization of α-vinyl naphthalene leads to isotactic P1VN which crystallizes in 4_1 helices. The valence angles of the polymer are $(\pi-\alpha_1)=(\pi-a_2) = 110°$, and the internal rotation angles $\phi_1 = 0°$ and $\phi_2 = 90°$. The σ-parameter for the isotactic polymer of $(-CHR-CH_2-)$ type can be calculated[18] if the energy ΔU of the transition from regular to an irregular sequence of monomer units is known. The general expression reduces to

$$\sigma^2 = 2 \cos^2(\alpha/2) \cot^2(\alpha/2) \exp(\Delta U/RT) \qquad (8)$$

From M_w(GPC) and at 30°C, we have σ = 1.764 and ΔU = 84 cal/mole. $D_r \times 10^4$, eq. (8), is then - 2.3 degree^{-1}, whereas the experimental value from Table VI is -18.7 to -16.3. This big discrepancy reflects once more the unreasonable value of σ. Substituting into eq. (8) alternatively σ = 2.457, ΔU = 475 cal/mole and $D_r \times 10^4$ = -26.1 to be compared with -7.7 to -13.6. The absence of information about the structural parameters of P2VN and PVB make a similar calculation impossible.

5. Temperature dependence of the viscosity at finite concentrations.

The intrinsic viscosity data have suggested a transition only for P2VN at $t_2 \simeq 50°C$. The question arise whether this transition persists at higher concentrations or whether it is characteristic of the isolated molecule. For this purpose a vacuum sealed system, see Fig. 1, was constructed, which reduced the error for the series of temperature measurements from 0.5% in the previous runs to 0.02 % for a given concentration. A summary of these experiments is shown in Fig. 5 and Table IV. To our surprise there appear two transition regions around approximately 20 and 50°C for P2VN. Moreover, the other polymers

as well exhibit two transitions, neither of which is apparent in the $[\eta]$-T function.

The concentration used in Fig. 5 are within the range of validity of the usual linear relation

$$\eta_{sp} = [\eta]c \ (1 + k_1[\eta]c) \qquad (9)$$

We have examined the consistency of the data from the sealed viscometer and those used for extrapolation to infinite dilution. Columns 7 and 8 of Table IV contain the values of $(\partial \ln k_1/\partial T)_M$ calculated from the data shown in columns 5 and 6 of the Table. The differential form of eq. (9) was used, substituting numerical values of $[\eta]$, k_1, c and D. For the temperature dependence of solvent and polymer densities the literature data[19] for benzene and PS were taken. The calculated temperature coefficients of k_1 above and below t_2 are in qualitative agreement with the trend of experimentally established k_1-values for the four samples investigated. It is interesting to compare the data for the two P2VN polymers. For both the coefficient in the upper temperature range is lower. However for the smaller molecular weight the lower value has a negative sign. This phenomenon can be seen as well from the actual data of k_1 (Table II). For the lower molecular weight samples k_1 has a maximum at $t \simeq 45°C$. Judging from the data of $(\partial \ln k_1/\partial T)_M$ as shown in Table IV, the maximum should not be expected for other PVAr.

In conclusion we believe that the transitions seen in Fig. 5 are real not only for P2VN were at least one transition for one of the two molecular weights is

observable by means of intrinsic viscosities, but also for all the other polymers. The phenomenon is magnified by concentration.

Correlations between the conformational parameter σ and the volume of the side group V_x have been reported in the literature[9]. In Fig. 11 we show the appropriate plot with our results at 30°C included. The upper line was drawn through PS with the slope given in Fig. 10, ref. 9 and derived from data on poly(alkyl methacrylates) and other polymers. The consistency with our results for P2VN and PVB as well as P1VN (M_w from light scattering) will be noted. The lower line refers to recent data on poly(1-olefins) As one could expect, polystyrene derivatives occupy an intermediate position.

6. Nuclear magnetic resonance of P2VN solutions

An attempt has been made to use NMR-high resolution spectroscopy as a more direct method for observation of macromolecular transitions. The measurements were considered preliminary   and only spectra of three solutions of P2VN-68 were taken. The results are summarized in Figs. 6 and 7. Due to the low temperature of the measurements and low tacticity of the sample we obtained broad line spectra which were treated similarly to spectra of solid polymers.

In both Figs. 6 and 7 two transitions (at $t_1 \simeq 20°C$ and $40 \leq t_2 \leq 50°C$) are visible. As expected, the half width increases with concentration and decreases with temperature, (Fig.6). The transitions affect aliphatic as well as aromatic protons. The change in the first case is much more pronounced. It is interesting that the half widths of $H_{7.44}$ and $H_{7.14}$ peaks at the same temperature are the same within   experimental error. This indicates

that the spin-spin relaxation time T_2 is the same for both -CHR-and
-CH$_2$- positions.

From the data shown in Fig. 6, using formulae of Gutowsky and Pake[20]
we calculate the activation energies E of the main transition motion at t_2=
50°C . The values for 7.6% and 11.8% solution are respectively
E = 1.9 ± 0.3 and E = 2.6 ± 0.5 kcal/mol, from which a value of 23 ± 7 kcal/mol
for pure polymer can be estimated by noting the approximate proportionality
of E with concentration. This high value of E indicates strong hindrance of
motion at t_2.

A slightly different picture is presented in Fig. 7. The height of the
peak is proportional to the RF-field,magnetic field H_1, spin-spin relaxation
time, T_2, and population of the nuclei, Π_o . Taking the ratio of the height
of the aliphatic peak to the aromatic peak we are in fact measuring the ratio
of the products $R_i = (\Pi_o T_2)_i / (\Pi_o T_2)_{Ar}$, i = α,β . As can be seen from Fig. 6,
the T_2 for both peaks at the same temperature are the same. The decrease of
$R_{7.14}$ and increase of $R_{7.44}$ with increasing temperature must be due to re-
spective changes of the population of the $H_{7.14}$ and $H_{7.44}$ peaks. It is worth
recalling also that the positions of the $H_{7.14}$ and $H_{1.75}$ peaks remain constant
with temperature, while $H_{7.44}$ is appreciably shifted upfield.

It is known that the change of the position of the proton relative to
the plane of an interacting aromatic group causes the change in the chemical
shift of the proton; placing a proton closer to the plane of an aromatic group
shifts its signal downfield. Thus, the change in population of $H_{7.14}$ and
$H_{7.44}$ peaks can be interpreted as an indication of the change in the position

of one of the β-protons in respect to the naphthalene rings. The change
causes a shift of one of the β-H signals to a lower field which is observed
as a shift in the apparent position of a $H_{7.44}$ peak and in the population
of absorbing nuclei. Higher values of σ and $(-D_r)$ are usually ascribed to
a stiffer polymer backbone chain. This and the NMR analysis suggest that at
the transition temperature the more rigid and closely packed structure is
disoriented. From the NMR studies the transition temperature t_2 for P2VN is
observed to be 40-50°C, similar to the viscometric results.

P2VN has been studied over a wide range of temperatures by Eskin et al[2c]
by means of different techniques. The authors found that in decalin P2VN exists
in two forms of different optical anisotropy. Here the transition region was
found to be t_2= 45-60°C.

CONCLUSIONS

We have presented evidence for partial stereospecificity in the case of our
P1VN-8036. As the sample has been polymerized in solution, this in fact is an in-
triguing observation: it implies either an orientation effect of the monomer on
addition to the growing chain or preorientation of monomer units in a solution
prior to polymerization. If this is true,tacticity should be expected in the case
of P2VN. On the other hand, a simple geometrical calculation shows that the β-
naphthalene group extends 9.2 Å from a backbone carbon atom. It is extremely dif-
ficult to pack such a macromolecule into a crystal, with a density not substantially
smaller than that of the amorphous region. A similar argument should be true for
PVB. The stereopolymerized but amorphous[4] P2VN gives support to this reasoning.

From the reported viscosity and NMR data we see that there are two, possibly three transition temperatures for PVAr solutions within the investigated t-range, $t_1 \simeq 20°C$, $t_2 \simeq 50°C$ and perhaps $t_3 \simeq 70°C$. The first, t_1, observed in respect to n_{sp}, Δ and (H_i/H_{Ar}) (the $[\eta]$-measurements were carried out for $t>20°C$) seems to be well established. The most pronounced change at t_2 has been reported previously[2c] and is apparent in all these quantities as well as in K_θ. Finally, the third, t_3, is noticeable only in (H_i/H_{Ar}) but not observable in Δ and something is seen in n_{sp} for P1VN, P2VN, and PS. It is noteworthy that the n_{sp}-transitions for PVAr and PS are located at the same temperatures t_1 and t_2 (see Fig. 5). A transition at $t_2 \approx 50°C$ is also observed for polymethyl methacrylate[21]. In polypropylene[10a] one can derive from $[\eta]_\theta$ $t_2 \approx 70°C$. In isotactic polystyrene $t_2 \approx 80°C$,[21,22] from a variety of dilute solution measurements. The close similarity in the numerical values of RT_2 is striking.

On the basis of the NMR spectra it is possible to differentiate the mechanisms of the three transitions. The first is the most pronounced on the Δ-t plot and in fact the broadening effect is larger than for t_2. The (H_i/H_{Ar})-t function shows no substantial change at t_1. In other words the transition changes the relaxation times of aromatic and aliphatic protons by the same order of magnitude, and does not introduce any substantial change in the relative population of nuclei, i.e. in the   configuration of the molecules. Judging by the magnitude of the decrease in Δ, the activation energy is very large.

In contrast the second transition appears to affect mostly methylene protons, both in respect to effective population and relaxation times. Whereas at $t<t_2$ the intensity of $H_{7.14}$ was smaller than the intensity of $H_{7.44}$, at $t>t_2$ the reverse situation is observed. From this observation and from the drift of the position of $H_{7.44}$ with t we have to conclude that one of the methylene hydrogens strongly hybridized by a naphthl group at $t<t_2$, is situated away from its plane at $t>t_2$. The aromatic hydrogens are only slightly affected. The transition requires a large activation energy (E = 23 ± 4 kcal/mol). Comparing this value with the activation energy at the glass transition, we note that it is about 1/4 - 1/5 that of polystyrene[23], although it is comparable with, for example, that of isotactic polypropylene[24].

There are two ways in which the β-H can move away from the Ar-plane: a) by rotation of the Ar-group, or b) by rotation of the -CHR-CH$_2$- backbone bond. The NMR studies of the solutions of PS and substituted PS allowed Bovey et al[6] to postulate a quasi-crystalline intermolecular stacking of phenyl groups in sequences exceeding 8-10 units. If the stacking of side groups exists in our P2VN solutions it must arise by piling up naphthyl groups of two parallel segments either of the same or of different chains (in the case when stacking would come from neighboring segments, the H_β would not be in a plane of Ar-groups). This is reasonable also from the point of view of the known helical structures[18] of PS and P1VN which should be similar to the structure of the tactic segments of P2VN in solution. In PS and P1VN the identity periods are 6.65 and 8.2Å respectively.

The latter is large enough to accomodate two aromatic rings of van der Waals thickness 3.6 $\overset{o}{A}$. This would account for the observed concentration dependence of Δ in P2VN, whereas Bovey et al[6] did not find such up to 50-60 wt % of PS. The transition t_2 at which the H_β escapes from the plane of naphthyl groups must be accompanied by a disorientation of the regular structure of tactic segments.

Concluding, our data confirm previous observations[2a] of the existence of a transition at $t_2 \simeq 50°C$ for P2VN and show that this phenomenon is of a general nature. Our numerical values of σ for PVAr are higher than those reported in the literature. They fit well on the $\sigma - V_x$ plot, Fig. 11, with a slope taken from the literature[9] which would tend to confirm at least their consistency. The line referring to the PVAr is moreover suggestive of a homologous series relationship.

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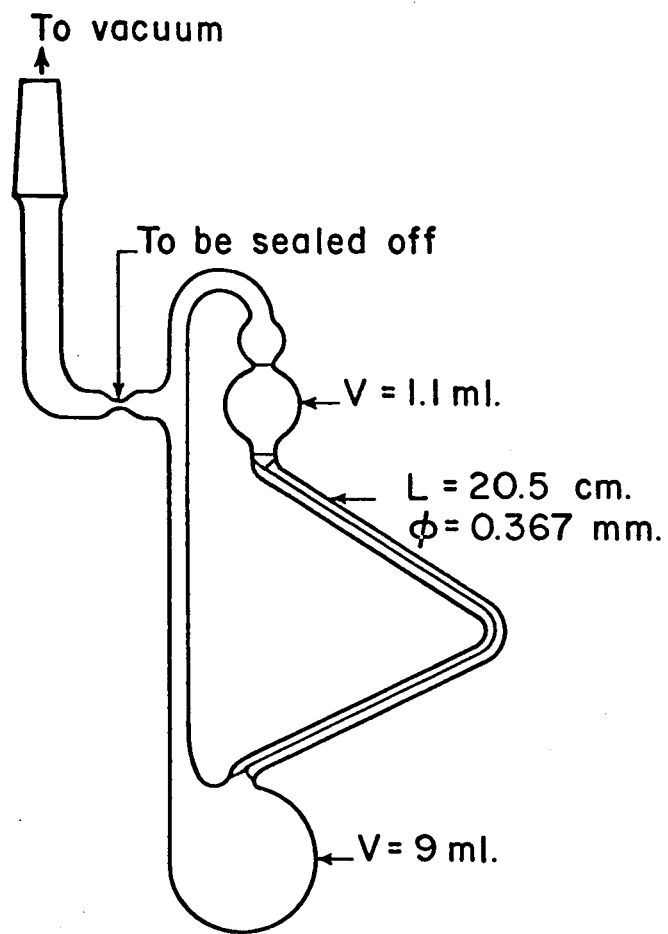
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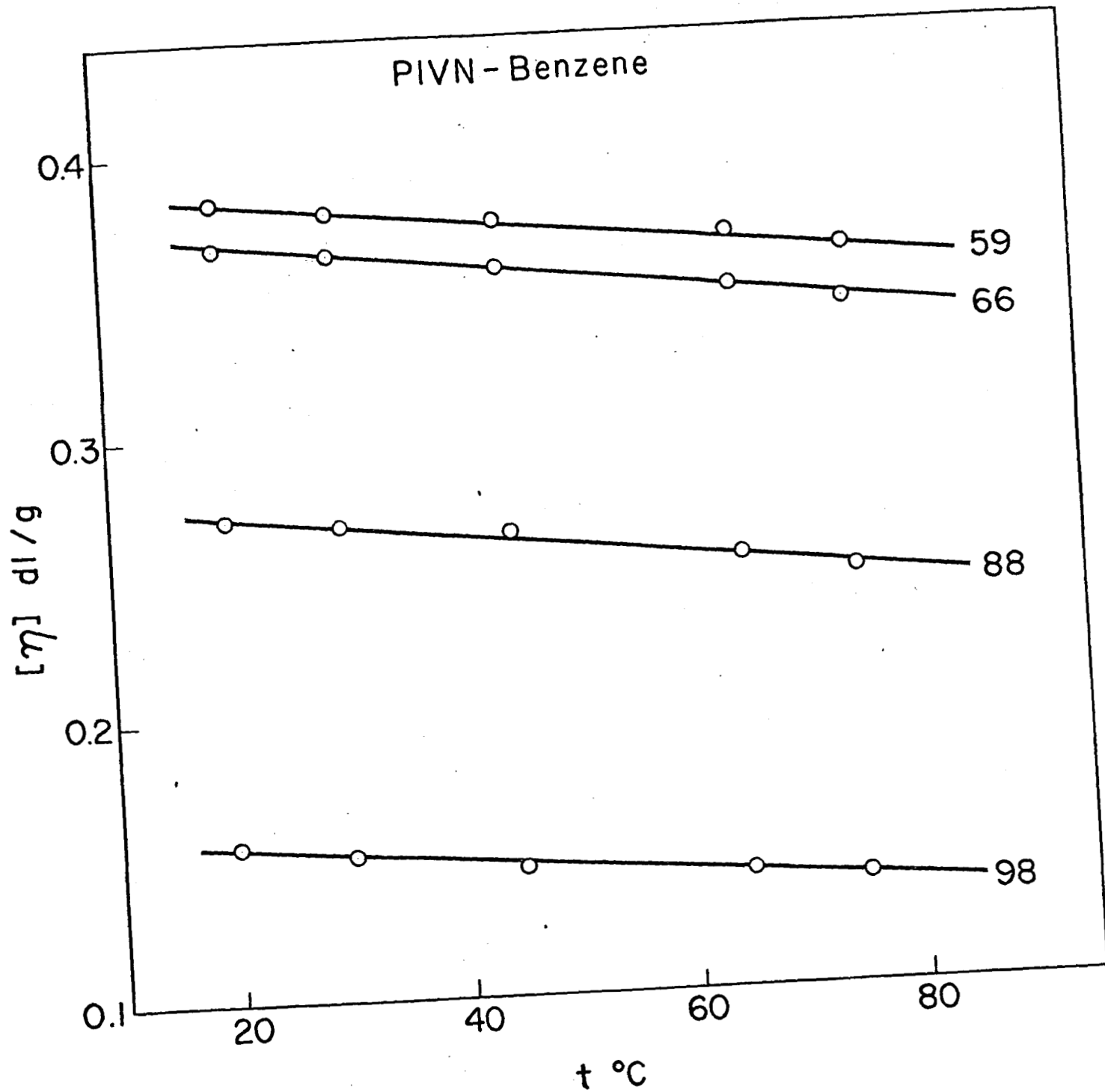
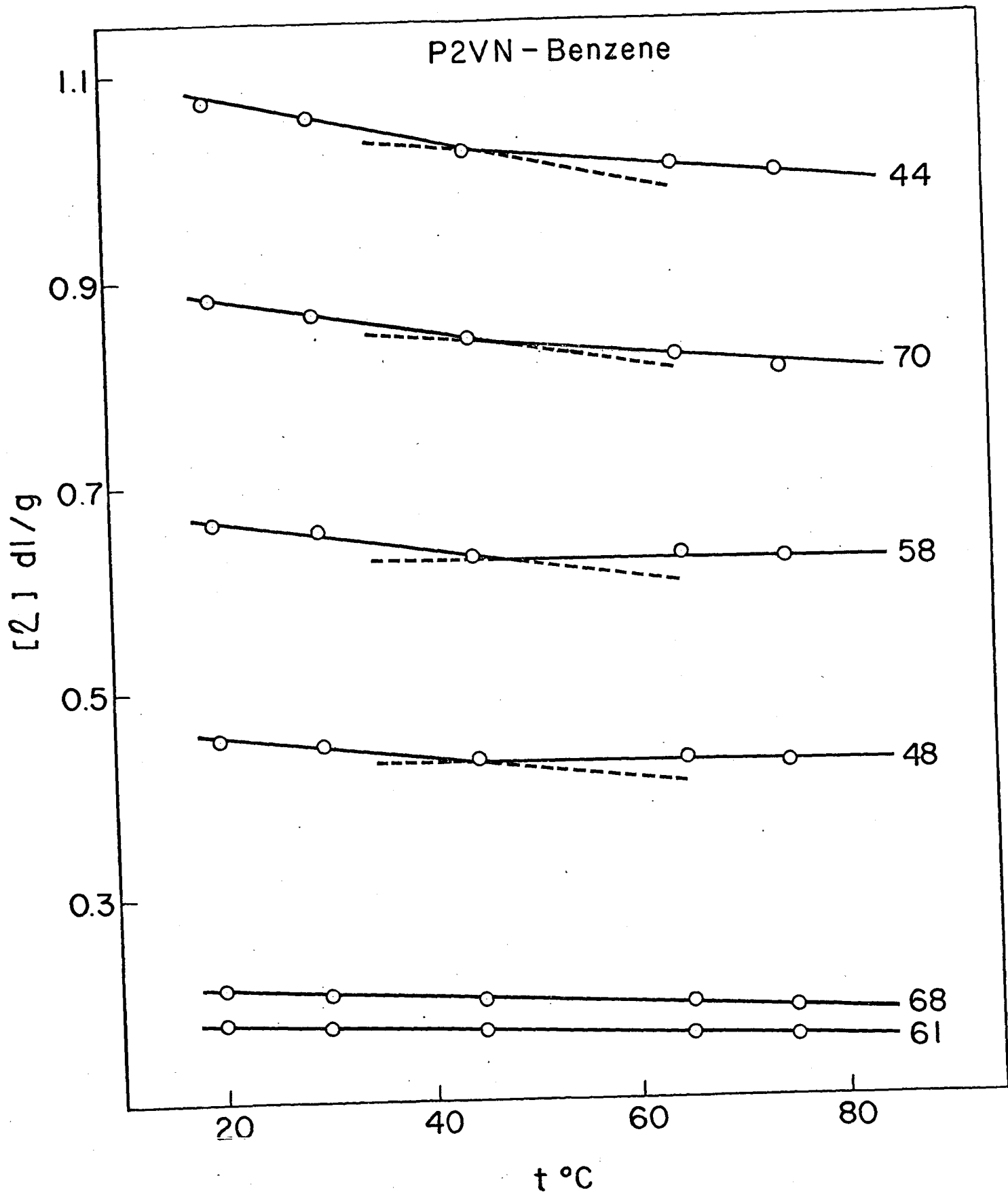   W.P.Slichter, J.Polym.Sci.,Part C, 14,33(1966)

LEGENDS FOR FIGURES

1   Sealed viscometer for determination of temperature coefficients of
    solution viscosity. V's are the volumes of the upper and lower
    bulbs, and L and ϕ length and diameter of the capillary.

2   Intrinsic viscosity of P1VN in benzene as a function of temperature.
    Numbers refer to sample symbols in Table I.

3   Intrinsic viscosity of P2VN in benzene as a function of temperature.
    Numbers refer to sample symbols in Table I.

4   Intrinsic viscosity of PVB in benzene as a function of temperature.
    Numbers refer to sample symbols in Table I.

5   log η_{sp} vs. 1/T for solutions of PVAr and PS . Concentrations are
    listed in Table IV. Note separate scale for each curve as indicated
    by respective code.

6   Temperature dependence of half width of $H_{7.44}$, $H_{7.14}$, $H_{1.75}$ peaks
    ascribed to β-protons, α-protons and aromatic protons for three so-
    lutions of P2VN-68 in CCl_4-dioxane (10:1) by volume.

7   Temperature dependence of the peak height ratios $H_{7.44}/H_{1.75}$ and $H_{7.14}/$
    $H_{1.75}$ of three solutions of P2VN-68.

8   Plot of Mark-Houwink-Sakurada constants K vs. a for PVAr in benzene at
    20° and 75°C. Bars refer to literature data. Numerical values from
    Table III.

9   Temperature dependence of K_{θ} for PVAr in benzene. Points calculated
    from eq.(4), lines drawn with slope computed from the data shown in Figs.
    2-4. The limiting value log $K_{\theta} = \lim_{a \to 1/2} \log K(a)$ as obtained from Fig. 8 is also

marked. Circles and solid lines calculated from M_w(GPC); squares

and broken lines from M_w(LSc).

10   Temperature dependence of the long range interaction parameter B

for PVAr in benzene. Circles and solid lines calculated from M_w(GPC);

squares and broken lines from M_w(LSc).

11   Conformational parameter σ as a function of the molar volume of pendant

groups V_x at 30°C for PVB, P1VN and P2VN. The upper line is drawn with

the same slope as in Fig. 10 of ref. 9. Symbols: PE-polyethylene, PP-

polypropylene, PB-polybutene-1, PCS-poly(p-chlorostyrene), PMS-poly

(p-methylstyrene), PDCS-poly(3,4-dichlorostyrene), PHS-poly(p-cyclohexylstyrene)
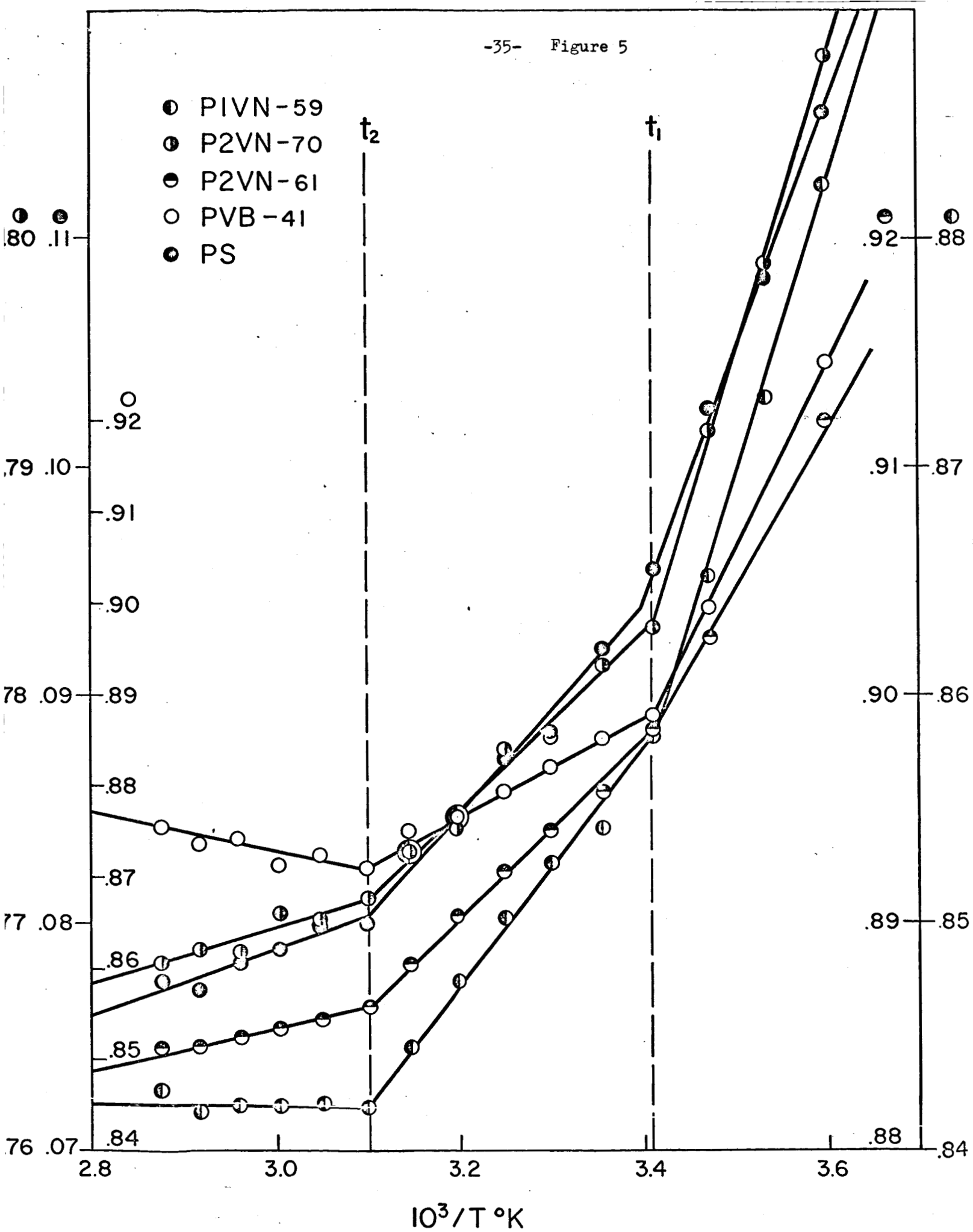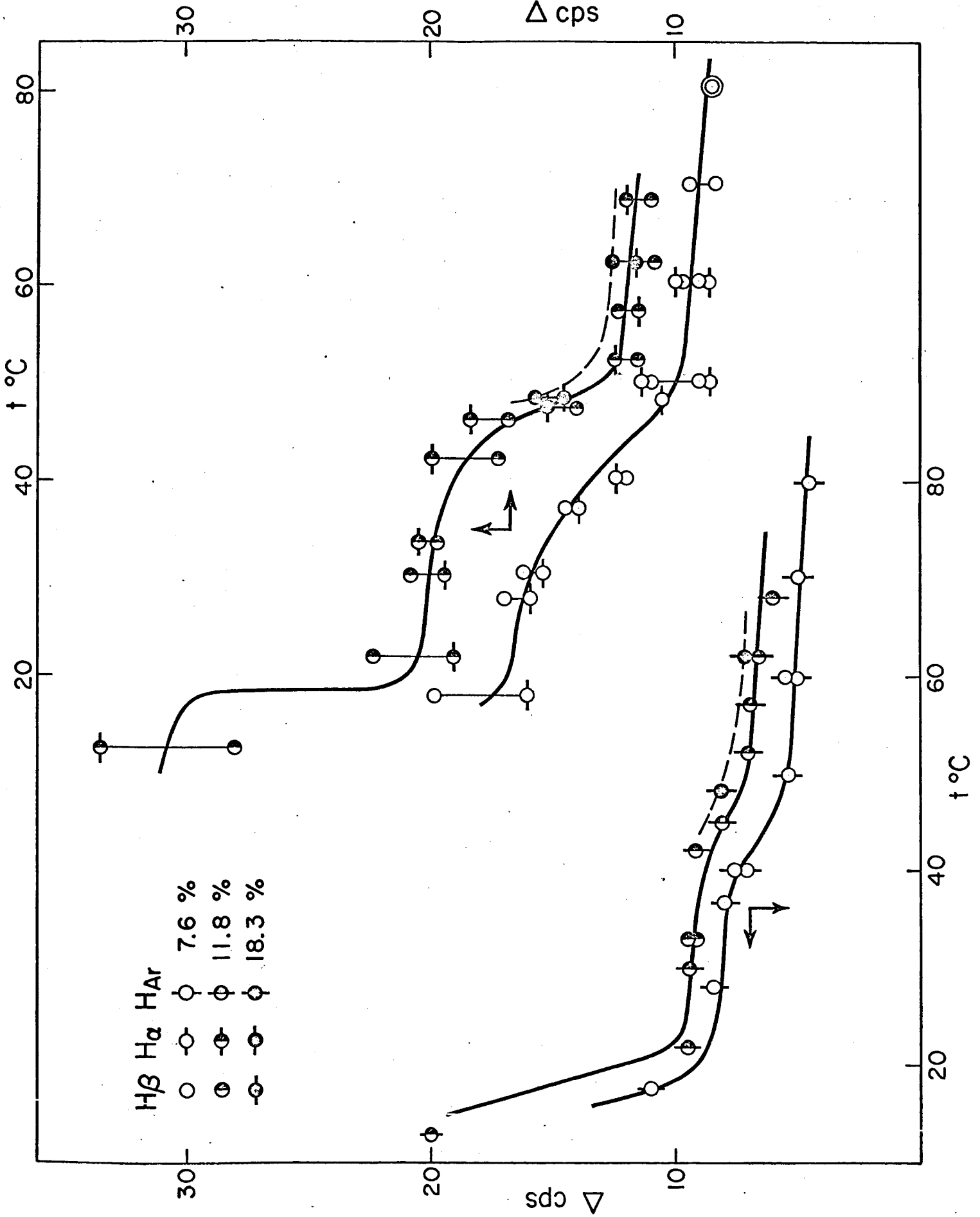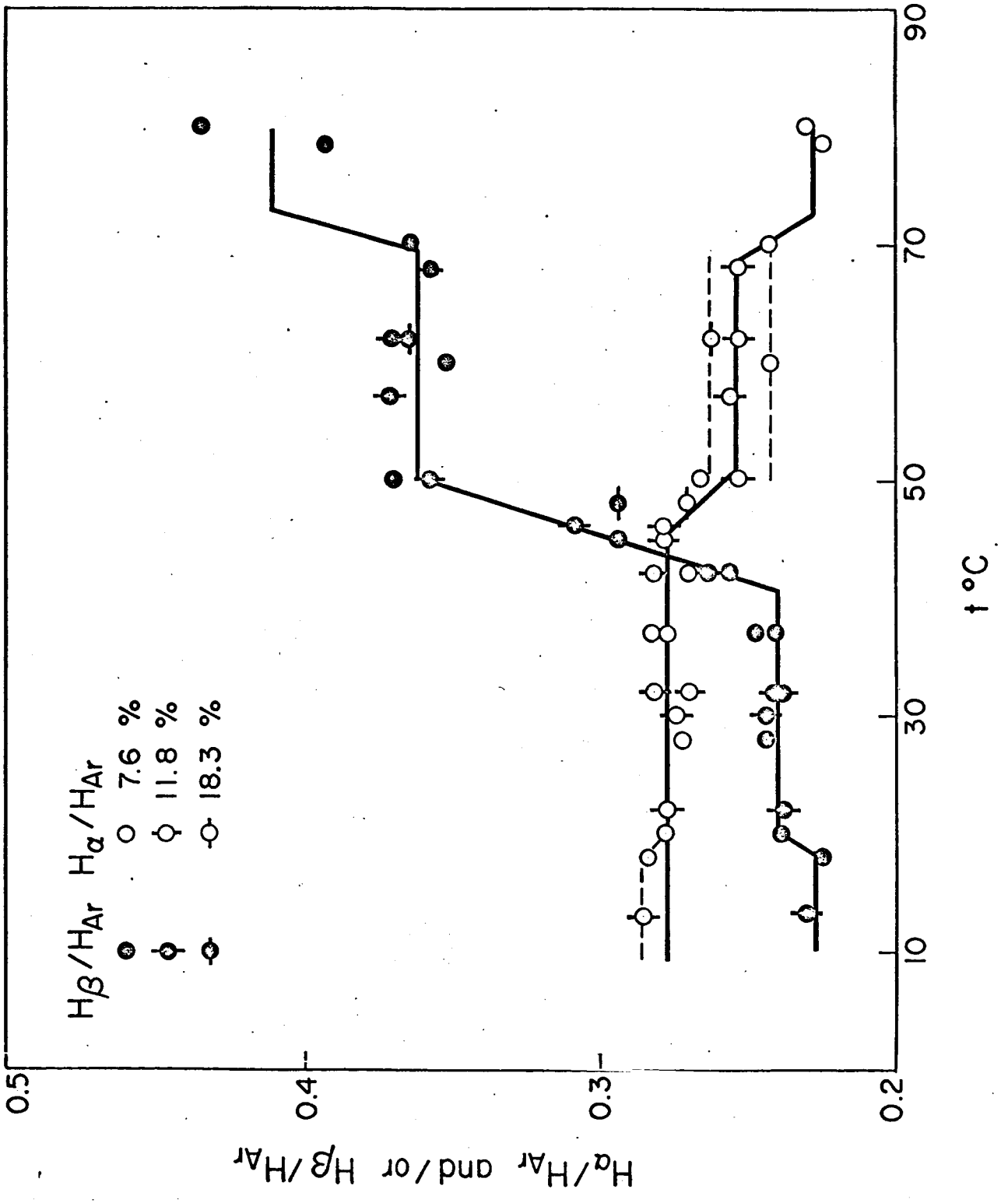
Squares calculated from M_w(LSc).

To vacuum

To be sealed off

$V = 1.1$ ml.

$L = 20.5$ cm.
$\phi = 0.367$ mm.

$V = 9$ ml.

Figure 2

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PIVN - Benzene

Figure 3

P2VN – Benzene

PVB in Benzene

-35-   Figure 5

Legend:
- ◑ PIVN-59
- ◐ P2VN-70
- ⊖ P2VN-61
- ○ PVB-41
- ● PS

x-axis: $10^3/T \,°K$

Figure 6

Figure 7

Figure 8

Figure 8

Figure 9

Figure 11

-41-

Figure 11