

Viscosity of Vinyl Aromatic Polymer Solutions

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Viscosity data are presented for benzene solutions of three vinyl aromatic polymers: poly(1-vinylnaphthalene), poly(2-vinylnaphthalene) and poly(vinylbiphenyl) at 30°C and in the range of concentration $c \leq 4/[\eta]$. The results are compared with those for polystyrene in a theta and a good solvent. The applicability of the superposition scheme developed earlier and the molecular weight dependence of the reducing parameters are examined. For reduced viscosities $\tilde{\eta} \equiv \eta_{sp}/c[\eta]$ below about 1.6, superposition is achieved for all molecular weights. Observed differences in the molecular weight range of validity of superposition at elevated concentrations for the systems considered can be correlated with chain stiffness and solvent-polymer interactions, as characterized by the parameter B . A new reduced variable \tilde{c}_1 is suggested for a comparison of the relative positions of the generalized viscosity functions, $\tilde{\eta} = f(\tilde{c}_1)$, of different polymer solutions. The relative positions of the curves appear to be related to the relative values of the long range interaction parameter B .

It has been shown that the viscosities of polymer solutions can be represented by general functions, independent of molecular weight, M

$$\eta_{sp}/c[\eta] \equiv \tilde{\eta}(\tilde{c}) \quad (1)$$

where $\tilde{c} \equiv c/\gamma'$, and the concentration parameter $\gamma' = \gamma'(M, T)$ is characteristic of the polymer-solvent system and independent of concentration c .

The above statement implies a principle of corresponding states and was first derived from an analysis of η/c data of polystyrene (PS) solutions in good and theta solvents¹. Later the principle was found to hold for PS-near-theta-solvent systems² and very recently proved to be valid for polyisobutene (PIB), polyvinyl chloride (PVC), polyvinyl alcohol, cellulose derivatives and polyisoprene solutions³. The viscosities for these twelve different polymer-solvent systems were measured in different laboratories, by different methods using samples of different heterogeneities. The representation proposed gave very good results in the whole range of concentrations (up to 50 per cent) for polymer-poor solvent systems. With increasing solvent power deviations in the lower molecular weight region were observed. These systems show analogous deviations in respect of their $[\eta]/M$ and $[\eta]/T$ relations. In the PS-toluene system we observed deviations for $M \leq 15\,000$, in PIB-isooctane for $M \leq 20\,000$, and in PVC-cyclohexanone for $M \leq 26\,000$.

In this paper we continue our investigations of concentrated systems and present η/c data for benzene solutions at 30°C for three vinyl aromatic polymers (PVAr), namely poly(4-vinylbiphenyl) (PVB), poly(1-vinylnaphthalene) (PIVN), and poly(2-vinylnaphthalene) (P2VN), in the range of

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concentrations $c \leq 4/[\eta]$ (g/dl). The η/c relations for these polymers can be compared directly with those for the PS-solvent systems¹. It is of particular interest to examine how the increased bulkiness of these aromatic side groups affects the polymer chain configuration, the solution behaviour and the range of validity of the general equation (1).

EXPERIMENTAL

The polymers were synthesized for the Jet Propulsion Laboratory by Dr J. Heller at Stanford Research Institute and received through the courtesy of Dr J. Moacanin. They were prepared by anionic polymerization, fractionated and characterized by gel permeation chromatography⁴ (GPC), which was calibrated using light scattering and osmotic data at the JPL. PVB and P2VN samples were reprecipitated in our laboratory from benzene solution by methyl alcohol and dried in a vacuum oven for two weeks at 50°C. Selected samples of these polymers measured before and after the precipitation showed no change in $[\eta]$ and in the Huggins parameter k_1 . For P1VN we found that additional purification was not needed. The characteristics of all samples are presented in *Table 1*.

Table 1. Characteristics of polymer samples

No.	Symbol	$M_w \times 10^{-3}$	M_w/M_n	$[\eta]^*$	Benzene k_1^*	30°C $(k_1[\eta])^{-1}$	γ
Poly(1-vinylnaphthalene)							
1	P1VN-59	155.3	1.14	0.387	0.43	6.01	1.00
2	P1VN-66	147.3	1.48	0.372	0.40	6.72	1.03
3	P1VN-88	103.4	1.05	0.270	0.46	8.05	1.31
4	P1VN-8036	52.2	1.06	0.156	0.50	12.82	1.69
Poly(2-vinylnaphthalene)							
5	P2VN-44	736.1	1.55	1.072	0.33	2.83	0.555
6	P2VN-70	563.4	1.88	0.880	0.36	3.16	0.660
7	P2VN-58	306.1	1.41	0.662	0.36	4.20	0.833
8	P2VN-46	182.5	1.29	0.453	0.42	5.26	1.00
9	P2VN-68	64.0	—	0.229	0.49	8.91	1.72
10	P2VN-61	48.9	—	0.204	0.50	9.80	2.02
Poly(4-vinylbiphenyl)							
11	PVB-63	1104.0	2.15	1.281	0.36	2.17	0.312
12	PVB-41	706.5	2.06	0.940	0.33	3.22	0.468
13	PVB-71	169.4	1.45	0.381	0.33	7.95	1.00
14	PVB-56	103.0	1.52	0.248	0.40	10.08	1.41
15	PVB-51	80.8	1.26	0.234	0.36	11.87	1.52
16	PVB-8036	10.5†	—	0.070	0.85	16.83	2.52

*Average of the values shown in *Table 3*.

†Ref. 4.

Mallinckrodt's analytical reagent grade thiophene-free benzene was further purified by rectification on a packed column over sodium wire. For all the experiments the middle fraction (b.pt = 80.0 to 80.1°C) from the same batch was used.

The polymer solutions were prepared one day before use in 10 ml volumetric flasks by heating the polymer-solvent mixture up to 50°C for ca. 30 minutes. Due to special care taken during the reprecipitation of

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polymer and the purification of the solvent, both components were dust-free and the solutions did not require filtration.

The viscosity measurements were carried out in a Hewlett-Packard Autoviscometer Model 5901B with constant temperature bath, Model 5910A, using Cannon-Ubbelohde dilution viscometers, calibrated by means of NBS standard viscosity oils. The viscometer constants are shown in *Table 2*. Kinetic energy and density corrections were applied to all individual measurements. We did not use any correction for a rate of shear dependence. From *Table 2* one can see that for all systems $\beta \leq \beta_{\max.} \approx \beta_{\text{crit.}}/10$, where $\beta_{\text{crit.}}$ is the characteristic quantity of shear above which $[\eta]$ starts measurably to decrease⁵. Thus we should not expect any deviation due to shear stress in the region of infinite dilution. As far as the higher range of c and η is concerned, the viscosity of the same solution ($\eta \approx 1.5$ cP) measured in either viscometer 1 or 2 had the same value within experimental error, indicating the absence of shear stress influence in this region as well.

Table 2. Characteristics of viscometers

No.	Cannon Inst. Co. Code	\bar{A}	\bar{B}	$G_{\max.} \times 10^{-3}/\text{sec}$	$\beta_{\max.}$
1	D-707/50	0.0041543	1.425	1.48	0.0261
2	D-442/100	0.013718	2.60	0.89	0.0158

Constants \bar{A} and \bar{B} from the relation $v(\text{cSt}) = \bar{A}\tau - \bar{B}/\tau$, where τ is the efflux time in seconds, $G_{\max.}$ and $\beta_{\max.}$ —maximum rate of shear and of the characteristic parameter of shear: $\beta_{\max.} \equiv (\eta)\eta_0 M/RT)G_{\max.}$ (η_0 is solvent viscosity).

For each viscosity/concentration curve at a given molecular weight, four initial solutions were usually prepared and these solutions subsequently diluted in the viscometer. The $[\eta]$ s were determined from separate sets of highly diluted initial solutions. To calculate each $[\eta]$ value two methods were applied: (1) using the viscometer constants \bar{A} and \bar{B} (*Table 2*) and the solution density, the viscosity of each solution was computed from its efflux time, τ . Using the solvent viscosity, $\eta_0 = 0.564$ cP, a plot of (η_{sp}/c) versus c was constructed. From this plot $[\eta]$ and k_1 were obtained directly. These values are shown in columns 3 and 4 of *Table 3*. (2) The second way of calculating $[\eta]$ had been proposed by one of the authors⁶: instead of applying the kinetic and density corrections to each individual τ value, the set of constants $[\tau]$ and $k_{1\tau}$ was calculated from the $(\tau - \tau_0)/(\tau_0 c)$ versus c plot (τ_0 is the efflux time of the solvent). From the values of $[\tau]$ and $k_{1\tau}$, $[\eta]$ and k_1 were calculated using the following equations:

$$[\eta] = [\tau] (1 + H)/(1 - H) + D$$

$$k_1 = k_{1\tau} (1 - H)/(1 + H) - H(1 - H)/(1 + H)^2 + [\eta] D \quad (2)$$

where $H \equiv \bar{B}/(\bar{A}\tau_0^2)$ and $D = 10^{-2}(d_0^{-1} - d_p^{-1})$. As usual $[\eta]$ is expressed in dl/g units, and d_0 and d_p are solvent and polymer densities in g/ml.

In columns 5 and 6 (*Table 3*) the $[\tau]$ and $k_{1\tau}$ data are shown and in columns 7 and 8 $[\eta]$ and k_1 calculated from these by equation (2). As can be seen, the agreement is quite good. The $[\eta]$ and k_1 data shown in *Table 1* are the averages of those shown in *Table 3*.

Table 3. $[\eta]$ and k_1 for vinyl aromatic polymers

No.	Polymer	$[\eta]$ (from η)	k_1 (from η)	$[\tau]$ (from τ)	k_{1r} (from τ)	$[\eta]$ eq. (2)	k_1 eq. (2)
1	PIVN-59	0.387	0.42	0.371	0.46	0.386	0.43
2	PIVN-66	0.373	0.40	0.356	0.43	0.370	0.40
3	PIVN-88	0.272	0.44	0.257	0.51	0.267	0.48
4	PIVN-8036	0.157	0.48	0.148	0.55	0.155	0.52
5	P2VN-44	1.072	0.32	1.041	0.36	1.073	0.33
6	P2VN-70	0.880	0.37	0.854	0.37	0.880	0.35
7	P2VN-58	0.663	0.36	0.639	0.39	0.660	0.36
8	P2VN-48	0.453	0.42	0.433	0.45	0.448	0.43
9	P2VN-68	0.230	0.49	0.219	0.52	0.228	0.49
10	P2VN-61	0.206	0.50	0.194	0.53	0.203	0.50
11	PVB-63	1.282	0.36	1.247	0.38	1.280	0.36
12	PVB-41	0.940	0.32	0.914	0.36	0.939	0.34
13	PVB-71	0.380	0.36	0.370	0.33	0.383	0.31
14	PVB-56	0.250	0.38	0.237	0.44	0.246	0.41
15	PVB-51	0.235	0.36	0.224	0.39	0.233	0.36
16	PVB-8036	0.070	0.84	0.064	0.90	0.070	0.86

RESULTS

The η_{sp}/c values obtained for the three polymers are exhibited in Table 4. The $\tilde{\eta}$ s [equation (1)] calculated from these data were plotted against c on a double logarithmic plot, and the curves obtained for the various M_w samples of each polymer were shifted along the c axis¹ to obtain the master curve of $\tilde{\eta} = \tilde{\eta}(\tilde{c})$ as shown in Figures 1 to 3. By this procedure values of

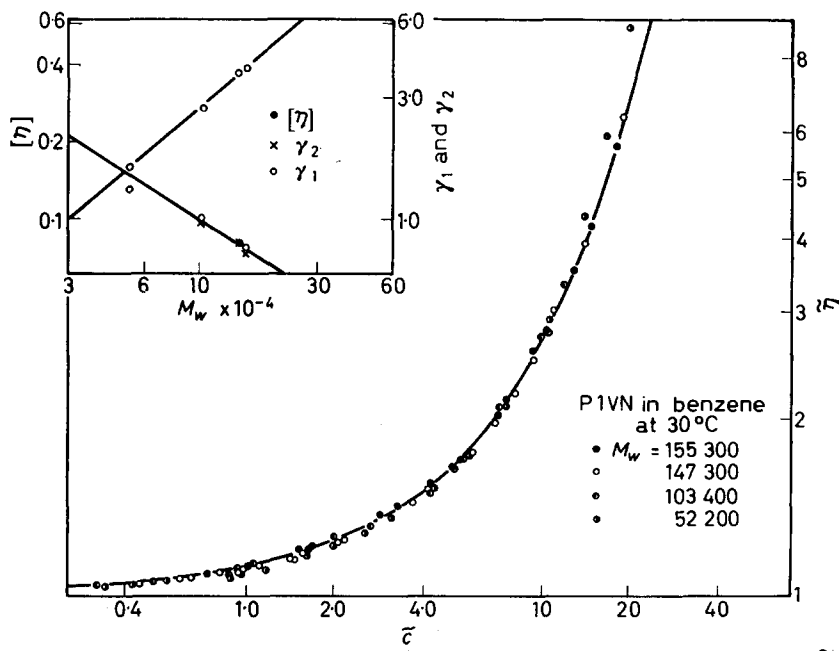


Figure 1—Reduced viscosity quantity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for P1VN in benzene at 30°C. Insert: $[\eta]$, reducing concentration factors γ_1 and γ_2 as functions of M_w

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Table 4. Viscosities of benzene solutions of vinyl aromatic polymers at 30°C

No.	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	c g/dl	η_{sp}/c dl/g	
Poly(1-vinylnaphthalene)													
	$M_w=52\ 200$		$M_w=103\ 400$		$M_w=147\ 300$			$M_w=155\ 300$					
1	0.4380	0.1628	0.3221	0.2822	0.3514	0.3906	0.5009	0.4196					
2	0.5475	0.1640	0.4920	0.2878	0.4838	0.3987	0.7927	0.4375					
3	0.7181	0.1669	0.7170	0.2947	0.6594	0.4083	1.2896	0.4689					
4	0.9382	0.1688	0.7493	0.2979	0.6737	0.4088	1.3207	0.4735					
5	1.2259	0.1717	0.9634	0.3018	0.7944	0.4142	2.2514	0.5325					
6	1.5544	0.1748	1.0940	0.3083	0.8928	0.4205	2.5767	0.5534					
7	2.1359	0.1839	1.5526	0.3236	1.1454	0.4325	3.3233	0.6048					
8	2.6342	0.1907	2.0432	0.3399	1.1804	0.4309	3.9412	0.6378					
9	3.3572	0.2003	2.7214	0.3626	1.2595	0.4408	4.1900	0.6576					
10	4.1486	0.2117	4.3587	0.4024	1.6622	0.4602	5.5722	0.7870					
11	5.7682	0.2384	5.5294	0.4591	1.7515	0.4641	5.9732	0.8300					
12	7.6550	0.2689	7.2494	0.5635	2.9249	0.5377	7.3462	1.0009					
13	10.167	0.3287	10.249	0.7357	3.4149	0.5630	8.1803	1.0802					
14	14.426	0.4564	12.276	0.8954	4.0981	0.6109	10.225	1.3612					
15	18.740	0.6755	—	—	4.7432	0.6512	11.673	1.6190					
16	22.296	0.9203	—	—	5.6105	0.7305	14.516	2.1923					
17	26.528	1.3973	—	—	6.5882	0.8143	—	—					
18	—	—	—	—	7.5586	0.9247	—	—					
19	—	—	—	—	8.6027	1.0350	—	—					
20	—	—	—	—	8.9162	1.1295	—	—					
21	—	—	—	—	11.418	1.4566	—	—					
22	—	—	—	—	15.414	2.3697	—	—					
Poly (2-vinylnaphthalene)													
	$M_w=48\ 900$		$M_w=64\ 000$		$M_w=182\ 500$			$M_w=306\ 100$		$M_w=563\ 400$		$M_w=736\ 100$	
1	0.6440	0.2192	0.6245	0.2464	0.3493	0.4834	0.2374	0.7046	0.2538	0.9512	0.2495	1.1731	
2	0.9056	0.2243	0.7780	0.2505	0.6036	0.5040	0.4482	0.7335	0.4242	1.0004	0.4094	1.2221	
3	1.3221	0.2326	1.2298	0.2624	0.8422	0.5297	0.6437	0.7656	0.5428	1.0358	0.4148	1.2407	
4	1.7840	0.2419	1.6069	0.2705	0.8969	0.5314	0.6984	0.7594	0.6217	1.0598	0.4289	1.2724	
5	2.4546	0.2545	1.6700	0.2728	1.1554	0.5578	0.8636	0.8007	0.7802	1.1096	0.5778	1.3064	
6	3.2498	0.2725	2.0461	0.2834	1.2098	0.5560	1.0313	0.8140	0.8832	1.1235	0.8041	1.3782	
7	4.3922	0.3031	2.7347	0.3001	1.3954	0.5800	1.2415	0.8590	1.1362	1.2092	0.9014	1.4330	
8	5.9305	0.3373	3.7563	0.3366	1.9615	0.6317	1.2629	0.8538	1.6620	1.3687	1.0852	1.5052	
9	10.334	0.4235	5.0589	0.3703	2.8604	0.7103	1.7091	0.9317	2.4275	1.5826	1.5927	1.7009	
10	14.498	0.5946	—	—	4.1921	0.8472	2.5170	2.3057	2.7593	1.6704	1.5927	1.7115	
11	—	—	—	—	6.3111	1.1438	2.5843	1.0798	3.5225	2.0179	2.2547	2.0331	
12	—	—	—	—	10.395	1.8922	3.0786	1.1825	4.4374	2.3503	3.0611	2.4636	
13	—	—	—	—	—	—	3.7891	1.3246	5.4777	2.9102	4.2072	3.2731	
14	—	—	—	—	—	—	4.6772	1.6207	—	—	5.9243	4.6467	
15	—	—	—	—	—	—	5.7134	1.8534	—	—	—	—	
16	—	—	—	—	—	—	9.3102	3.0244	—	—	—	—	
(Poly 4-vinylbiphenyl)													
	$M_w=10\ 500$		$M_w=80\ 800$		$M_w=103\ 000$			$M_w=169\ 400$		$M_w=706\ 500$		$M_w=1\ 104\ 000$	
1	1.9661	0.07843	0.8694	0.2533	0.3356	0.2570	0.2938	0.3939	0.1124	0.9788	0.2004	1.4004	
2	3.6604	0.08542	1.3468	0.2611	0.4677	0.2597	0.5534	0.4061	0.1506	0.9793	0.2952	1.4606	
3	5.6546	0.09458	2.1921	0.2793	0.5034	0.2632	0.6761	0.4209	0.2333	1.0020	0.3571	1.4945	
4	8.2120	0.1080	2.7695	0.2903	0.7085	0.2668	0.7555	0.4175	0.2979	1.0199	0.4385	1.5418	
5	10.784	0.1250	3.0641	0.3014	0.8954	0.2690	0.9278	0.4256	0.4179	1.0547	0.5999	1.6391	
6	15.205	0.1632	3.7148	0.3168	1.0643	0.2758	1.0358	0.4396	0.5268	1.0945	0.7587	1.7312	
7	20.132	0.2287	4.6201	0.3436	1.3353	0.2827	1.4064	0.4597	0.7700	1.1814	0.9433	1.8400	
8	24.901	0.3366	6.7231	0.4010	1.7087	0.3013	1.9226	0.4898	0.7846	1.1701	1.2186	2.0034	
9	—	—	8.2061	0.4566	2.3518	0.3112	2.5449	0.5292	0.9993	1.1962	1.6907	2.3430	
10	—	—	10.405	0.5502	3.0162	0.3295	3.3915	0.5582	1.2047	1.3169	1.8938	2.3819	
11	—	—	13.391	0.7140	3.7920	0.3528	3.3918	0.5806	1.4943	1.3832	2.3155	2.6870	
12	—	—	16.085	0.9289	4.9546	0.3917	4.7061	0.6519	1.7560	1.4828	2.4314	2.7877	
13	—	—	19.089	1.2226	6.5424	0.4489	5.8178	0.7354	2.1459	1.7071	2.9928	3.2615	
14	—	—	20.925	1.4872	6.6276	0.4519	6.6585	0.8030	2.3170	1.6572	3.6900	3.8596	
15	—	—	—	—	7.6855	0.4837	6.6665	0.8092	2.9324	1.8582	4.0555	4.1615	
16	—	—	—	—	7.8797	0.4998	8.2487	0.9635	3.5829	2.1038	5.0576	5.4463	
17	—	—	—	—	9.2756	0.5739	10.335	1.1982	3.7595	2.1671	—	—	
18	—	—	—	—	9.4266	0.5787	12.143	1.5152	4.6617	2.5349	—	—	
19	—	—	—	—	11.513	0.6995	—	—	4.8344	2.6368	—	—	
20	—	—	—	—	13.770	0.8648	—	—	5.9437	3.1292	—	—	
21	—	—	—	—	16.598	1.1044	—	—	6.1664	3.3310	—	—	
22	—	—	—	—	—	—	—	—	8.1869	4.4842	—	—	
23	—	—	—	—	—	—	—	—	11.123	7.4864	—	—	

the shifting parameter γ' were obtained, using a separate reference molecular weight M' for each polymer series: i.e. $\gamma'(M') \equiv 1$. The values of γ' are listed in column 8 of Table 1. In Table 5 we present the numerical values of the parameters α , α_1 , K and K_1' defined by the relations

$$[\eta] = KM^\alpha; \quad \gamma' = K_1' M^{-\alpha_1} = (M'/M)^{\alpha_1} \quad (3)$$

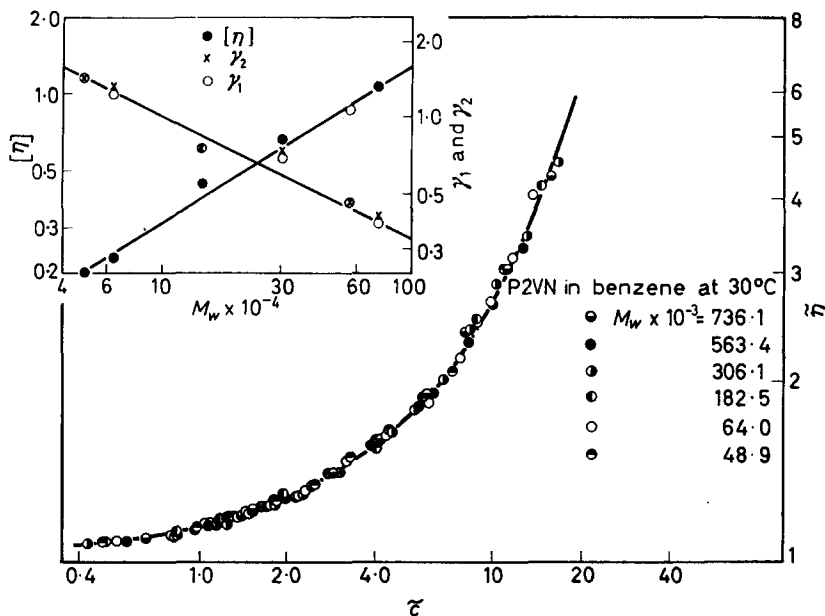


Figure 2—Reduced viscosity quantity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for P2VN in benzene at 30°C. Insert: $[\eta]$, reducing concentration factors γ_1 and γ_2 as functions of M_w

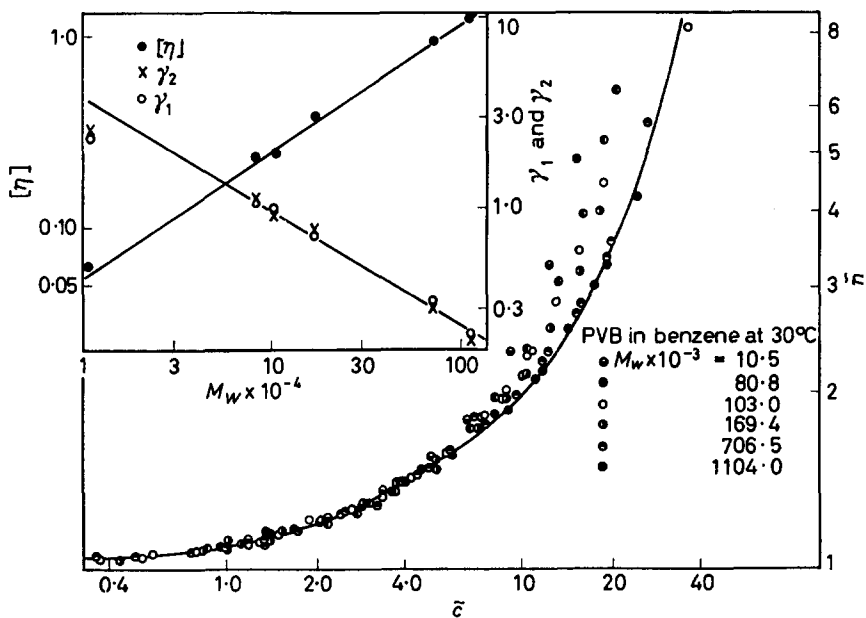


Figure 3—Reduced viscosity quantity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for PVB in benzene at 30°C. Insert: $[\eta]$, reducing concentration factors γ_1 and γ_2 as functions of M_w

Choosing now a common reference molecular weight for all systems, $M_1 \equiv 10^5$, and defining $\gamma_1(M_1) \equiv 1$, we have the analogous relation $\gamma_1 = K_1 M^{-a}$, with $K_1 = M_1^a$. In contrast to γ' the γ_1 's for different polymer-solvent systems can be compared with each other.

In the above relations the absolute values of γ' or γ_1 depend on the choice of the reference molecular weight. In the previous papers of the series¹⁻³ we have shown that as a consequence of the superposition principle, a parameter γ_2 may be defined by the relation

$$\gamma_2 = C / (k_1 [\eta]) \quad (4)$$

where the numerical value of the constant C depends solely on the choice of the reference molecular weight for $\gamma_2 = 1$. Setting $\gamma_1 = \gamma_2$ we compute the C values for solutions of each polymer. The root mean square error in C is five per cent. The average values of C for PVA and PS are shown in *Table 5*. Using these C values the individual values of γ_2 can be calculated. Their molecular weight dependence is shown in the inserts of *Figures 1 to 3* along with the molecular weight dependence of γ_1 and $[\eta]$. As one can see, γ_1 and γ_2 are scattered at random along the lines corresponding to equation (3), indicating the validity of equation (4).

DISCUSSION

(1) *Applicability of superposition principle*

We define $M_{\text{crit.}}$ as the lowest molecular weight of a given polymer-solvent system, for which a single reduced function $\tilde{\eta} = \tilde{\eta}(\tilde{c})$ can be specified over the whole available range of concentration. Similarly for $M \leq M_{\text{crit.}}$ let $\tilde{\eta}_{\text{crit.}}$ be the maximum value of $\tilde{\eta}$ which still obeys the superposition principle.

An examination of the reduced viscosity functions, *Figures 1 to 3*, reveals the following features. At sufficiently low reduced concentrations, $\tilde{c} \leq 6$, say, superposition is obtained for all molecular weights considered. At larger \tilde{c} , differences between the polymer series become apparent. Consider P2VN and PVB where the M range is similar. In the latter, increasing departures from the general relation with increasing \tilde{c} occur for $M_w < M_{\text{crit.}} \approx 169\,000$, whereas no systematic deviations are observable for the former. The molecular weight range of P1VN studied is narrow, but deviations may be noted for the lowest fraction, $M_w = 52\,200$. The concentration range, preparation and treatment of the solutions were identical and the solvent conditions at the single temperature used not too different. We may enquire therefore whether a correlation exists between the above differences and differences in the intrinsic chain conformations and solute-solvent interactions.

For this purpose consider the short and long range interaction parameters σ and B :

$$\sigma = (\langle r_\theta^2 \rangle / \langle r_{0f}^2 \rangle)_{N=\text{const.}}^{1/2}$$

$$B = (1/4\pi^{3/2}) (N^2 \bar{\beta} / 2M^2)$$

where $\langle r_0^2 \rangle$ and $\langle r_{0f}^2 \rangle$ are the mean square end-to-end distance of the unperturbed and freely rotating chain respectively, N is the number of chain carbon atoms, $\bar{\beta}$ the double cluster integral and the other symbols have their usual meanings. The recently calculated σ and B values of PVAr⁷ and PS at 30°C are shown in *Table 5*.

Table 5. Solution parameters of PVAr and PS

No.	Polymer	Solvent	Temp. °C	$K \times 10^4$ dl/g	a	K_1'	a_1	C eq. (4)	$M_{crit.}$ $\times 10^{-4}$	$N_{crit.}$	σ^*	B^* ($\times 10^{21}$) cm ³	σ^*C
1	P1VN	benzene	30	1.22	0.67	849	0.56	0.122	> 52.2	> 678	—	—	—
2	P2VN	benzene	30	1.48	0.66	481	0.50	0.143	‡	‡	2.95	0.47	2.10
3	PVB	benzene	30	2.95	0.59	639	0.53	0.101	169	1880	2.63	0.35	1.81
4	PS†	cyclo- hexane	34.4	9.02	0.50	260	0.47	0.170	< 15	< 288	2.20	0.00	1.81
5	PS†	toluene	30	1.18	0.71	1955	0.64	0.196	15	288	2.20	1.76	1.96

†ef. 7
 ‡ef. 1
 below range studied

In *Table 5* we also show the value of $M_{crit.}$ which is a measure of the validity of our superposition method; the higher the value of $M_{crit.}$ the less applicable the method for the polymer-solvent system.

No results are given for P1VN. The calculation based on a linear plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ yields $\sigma = 1.8$ when the molecular weights in *Table 1* are used. This value is unreasonably small. For P2VN and PVB M_w s, determined by GPC and light scattering⁴ respectively, yield σ s which agree within two per cent, provided the lowest molecular weight for P2VN and the highest for PVB are omitted. These two values deviate markedly from the linear relationship. On the other hand, for P1VN M_w from light scattering leads to $\sigma = 2.4$. This is reasonable but at complete variance with the result derived from GPC. The narrow range of molecular weights does not permit further analysis.

Because of the limited number of fractions we cannot establish precise numerical values of $M_{crit.}$. However, a parallelism between $M_{crit.}$ and σ is noticeable in *Table 5*. For the present agreement only the relative order, but not the absolute magnitude of σ is pertinent. An increase of σ results in a larger $M_{crit.}$. That is, departures from superposition at elevated concentrations already appear at relatively elevated molecular weights. This conclusion is not altered by the use of chain lengths $N_{crit.}$ in *Table 5*, since they also appear to be extremely sensitive to changes in σ in the vinyl aromatic series. Comparisons should strictly be made at closely similar long range interactions. $M_{crit.}$ is apparently less sensitive to variations in B than in σ , but studies of polyvinyl aromatics in theta solvents and of very low molecular weights ($M < 15\,000$) of PS in cyclohexane are desirable. For the latter polymer we note a decrease of $M_{crit.}$ with decreasing B and recall analogous observations for other polymers³.

Not surprisingly, of course, the parameter σ is not sufficient to characterize the limits of superposition in widely different polymer systems. For example, for polyisobutylene⁸ $\sigma = 1.8$, whereas $N_{crit.} \approx 360$ in isooctane.

We have referred to the range of molecular weights $M > M_{crit.}$ over which superposition applies. It is noteworthy also that in the polyvinyl aromatic

series the departures occur in a considerably lower range of reduced viscosities than for other polymers³, where $\tilde{\eta}_{crit.}$ exceeds at least five.

(2) *The concentration parameter γ'*

In a suspension of hard spheres the obvious measure of the reduced concentration is ϕ/ϕ_{cp} , where the ϕ s are volume fractions and the subscript 'cp' signifies close packing. Hence by analogy γ' , equation (1), may be considered to be proportional to an effective packing volume of the polymer coils. As for the molecular weight dependence, the inequality $a > a_1$ has been observed earlier in good solvents¹⁻³. Table 5 indicates a similar relationship for the polyvinyl aromatics studied here.

The absolute magnitude of γ and hence of C , equation (4), depends on the arbitrary choice of a reference molecular weight. The dimensionless parameter C , of course, is independent of molecular weight. Judging from the not too different initial slopes of curves 4 and 5, Figure 4¹, and Table 5,

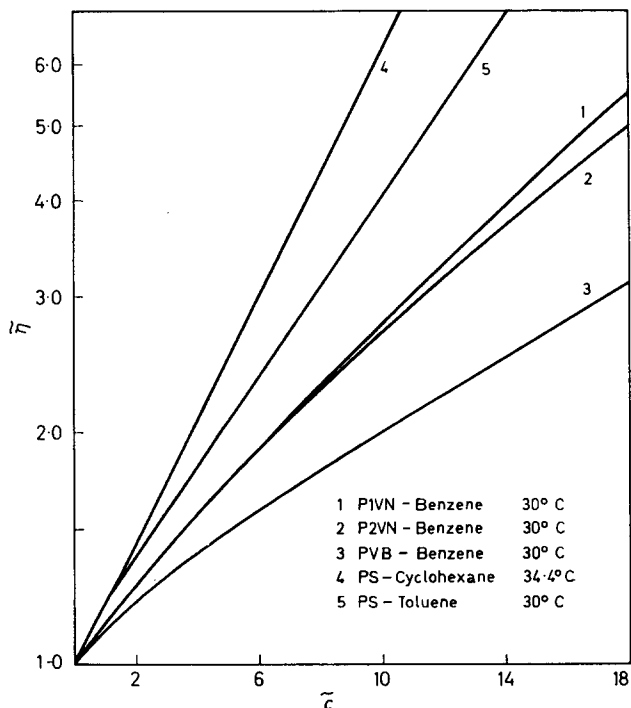


Figure 4—Semilogarithmic plot of reduced viscosity quantity $\tilde{\eta}$ as a function of reduced concentration \tilde{c} for PS-cyclohexane: $T=\theta$ (curve 4)¹, PS-toluene 30°C (curve 5)¹, P1VN-benzene 30°C (curve 1), P2VN-benzene 30°C (curve 2), PVB-benzene 30°C (curve 3)

C is weakly dependent on solvent power, but this observation deserves further study. Again, there is a more pronounced variation with σ . It is suggestive to treat C as a ratio between two characteristic coil volumes and

to consider its dependence on σ^3 . In *Table 5* it is seen that the product $C\sigma^3$ is reasonably constant. No significant improvement of this constancy would result from the use of a viscometric coil volume and the quantity $\sigma^3\alpha^n$, where $n \leq 3$ and α represents the polymer coil expansion factor. This may be another indication that the effective packing volume in our concentration range is principally determined by the unperturbed coil dimensions and only secondarily by polymer-solvent interactions.

(3) *Relative position of reduced curves*

The master curves, $\tilde{\eta} = \tilde{\eta}(\tilde{c})$, of the five polymer-solvent systems, based on γ_1 , are plotted in *Figure 4*. Generally speaking, their relative positions are paralleled by the relative values of the conformational parameter σ , of $M_{\text{crit.}}$ and M_0 . The variation with M_0 arises from the fact that for a given M and hence γ_1 , the chain length is smaller for the larger M_0 . Since the dependence of η_{sp}/c on chain length is greater than that of $[\eta]$, $\tilde{\eta}$ is smaller. For constant M_0 , we observed¹⁻³ earlier an increase in the derivative $d\tilde{\eta}/d\tilde{c}$ at sufficiently large \tilde{c} with decreasing solvent power; compare for example curves 4 and 5 (*Figure 4*). A similar pattern is indicated by P1VN and P2VN in benzene.

In an attempt to isolate the effect of long range interactions on the derivatives $d\tilde{\eta}/d\tilde{c}$, we account for the differences in monomer mass and chain stiffness by the introduction of the reduced concentration

$$\tilde{c}_1 = (c/M_0)/(\gamma\sigma^3) = \tilde{c}/(M_0\sigma^3) \quad (6)$$

The placement of the factor σ^3 is consistent with the approximate constancy of $C\sigma^3$ in equation (4). If γ is normalized by the chain length $N_1 = M_1/M_0$, $\gamma(N_1) = 1$, then $\gamma \equiv \gamma_1$. Consider now the comparative values of $(\tilde{c}_1 \times 10^2)$ for a fixed value of $\tilde{\eta}$, say, 3.5 in *Figure 4*. They are in decreasing order 1.60, 1.25, 1.22 and 1.18 for the systems 5, 3, 4, 2 respectively. The corresponding values of $(B \times 10^{27})$ in *Table 5* are 1.76, 0.35, 0.00 and 0.47. The order of the two quantities is the same except for system 2, P2VN-benzene, where we should have expected $0.0125 < \tilde{c}_1(\text{P2VN}) < 0.0160$. Actually, were we to put $\sigma = 2.40$, the value derived from the light scattering M_w , instead of $\sigma = 2.45$, \tilde{c}_1 would be increased to 0.0126.

Certainly, the suggestion made here in connection with equation (6) requires scrutiny by means of accurate σ and B determinations on these and other polymer-solvent systems.

CONCLUSION

The *range* of applicability of the proposed method of superposition of viscosity/concentration data is limited for polyvinyl aromatics compared with that for polystyrene. The limiting factors seem to be mainly the chain stiffness indicated by the magnitude of the conformational parameter σ for a given series of polymers and to a lesser extent polymer-solvent interactions. An increase in chain extension, due to either the first or the second factor, results in an increase of the limiting molecular weight above which a

principle of corresponding states is obeyed over the *whole* range of concentration explored here. It appears that $M_{\text{crit.}}$ and the effective packing volume of the polymer coils within a homologous series as derived from γ , depend mainly on short range interactions. In this context it would be highly desirable to examine systems containing stiff polymer chains, for example 1,4-polydienes, ribbon and ladder type polymers, polymers with aromatic groups in the main chain, etc. Unfortunately there are no such data available in the literature.

The effects of the short and long interaction parameters on the position of the general curves (for $M \geq M_{\text{crit.}}$) can be separated by using a reducing concentration \tilde{c}_1 defined in equation (6). An increase of B tends to decrease $\tilde{\eta}$ for the same \tilde{c}_1 .

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