

# The Influence of the Solvent Upon the Low Shear Viscosity of Styrene–Acrylonitrile Copolymer Solutions

R. F. BLANKS and B. N. SHAH, *Department of Chemical Engineering, Michigan State University, East Lansing, Michigan 48824*

## Synopsis

This paper describes the results of an experimental investigation concerning the effect of polymer–solvent thermodynamics on low-shear viscosity of copolymer solutions. Thermodynamic parameters and low-shear solution viscosities were measured for solutions of polystyrene homopolymer and styrene–acrylonitrile copolymers in four solvents: benzene, dioxane, methyl ethyl ketone, and dimethylformamide. The thermodynamic quality of a solvent for a polymer is characterized by free-energy-of-mixing parameters. These quantities are: the Flory-Huggins thermodynamic interaction parameter  $\chi$ , the second virial coefficient (from light scattering), the intrinsic viscosity, and the polymer expansion factor. The thermodynamic interaction between a solvent and a polymer in solution influences the rheological behavior of the system. At low concentrations of polymer in solvent, the low-shear solution viscosity is larger in a good solvent than in a poor solvent. In solutions of higher concentration, the reverse may be true and the viscosity is often significantly larger in a poor solvent than in a good one. These results are not predicted quantitatively by existing theory. The parameters in existing viscosity correlation techniques are found to be solvent dependent. The so-called entanglement concentrations for polymer solutions are not unique for a particular polymer but are related to the free energy of mixing polymer with solvent.

## INTRODUCTION

The viscosity of solutions of a macromolecule in a solvent is a function of the concentration and molecular weight of the macromolecule, the temperature of solution, the shear rate of measurement, and the molecular structures of the solvent and the macromolecule. The structure of a macromolecule affects the unperturbed dimensions of the molecule in solution owing to the influence of structure upon chain flexibility and intramolecular forces. The structures of the macromolecule and of the solvent affect the excluded volume and the volume of solution occupied by a polymer coil owing to the influence of structure upon thermodynamic interactions and free energy of mixing. These structural effects influence solution viscosity. The dependence of the polymer solution viscosity function upon shear rate, temperature, and polymer molecular weight has been the subject of many investigations.<sup>1–3</sup> The dependence of the viscosity function of moderately concentrated polymer solutions upon concentration and free energy of mixing has received less attention.<sup>2–4</sup> In this work we are interested in the dependence of the viscosity of polymer solutions upon polymer concentration and polymer–solvent thermodynamics.

When measured at low shear rate, the viscosity of most polymer solutions approaches a constant value  $\eta_0$ , the low-shear viscosity. In this discussion we shall also refer to the quantities  $\eta_{r0}$  and  $\eta_{sp0}$ , the relative and specific low-shear viscosity, respectively;  $\eta_{r0} = \eta_0/\eta_s$  and  $\eta_{sp0} = \eta_{r0} - 1$ , where  $\eta_s$  is solvent viscosity.

At very low concentrations of polymer in solvent, the polymer chains are believed to exist as isolated clouds of polymer segments which do not interpenetrate with each other. This model results in the following equation:

$$\eta_{r0} = 1 + cKM^a \quad (1)$$

where  $c$  is polymer concentration and  $K$  and  $a$  are constants determined experimentally for a particular polymer-solvent system. Polymer structure and system thermodynamics are reflected in the values of the parameters  $K$  and  $a$ . The parameter  $a$  varies from 0.5 in a thermodynamically poor solvent to 0.8 for a good solvent. This dilute solution model has been extensively verified.<sup>6-8</sup>

As the concentration of polymer in solution is increased, the polymer molecules overlap and become entangled. When this happens, the low-shear relative viscosity of the solution depends much more strongly on polymer concentration and molecular weight than in eq. (1):

$$\eta_{r0} \sim (cM^b)^\beta \quad (2)$$

Experimentally  $\beta$  is often found to have a value near 5 and  $b$ , a value near 0.68, so that correlations of the type  $\eta_{r0} \sim c^5M^{3.4}$  are frequently successful.<sup>9,10</sup>

The value of the product  $cM$  where eq. (1) ceases to describe the low-shear relative viscosity of a solution and where eq. (2) provides a reasonable fit is termed the critical entanglement density for a particular polymer-solvent pair. Below the critical entanglement density, the size and concentration of effective polymer spheres in solution dominate the flow phenomena, and eq. (1) applies. Above the critical entanglement point, the network structure of the solution is usually presumed to dominate the flow phenomena, and eq. (2) is used. Since the physical nature of the entanglements is usually thought to dominate the flow phenomena in concentrated polymer solutions, thermodynamic parameters are often neglected in this region.<sup>11</sup>

In recent years it has become clear that, while extremely useful for correlating  $\eta_{r0}$  for a particular polymer-solvent pair, eqs. (1) and (2) and the concept of a critical entanglement density are inadequate in predicting and correlating the viscosity-concentration function for one polymer in several thermodynamically different solvents. For polystyrene and poly(methyl methacrylate), several experimental studies have shown that whereas  $\eta_{r0}$  is higher for good solvents than for poor solvents at low concentration,  $\eta_{r0}$  may be several orders of magnitude higher in poor solvents than in good solvents at higher concentrations.<sup>4,12,23,25</sup> For a particular polymer the slope of the solution viscosity-concentration curve and the critical entanglement density are thus solvent dependent. This type of behavior was discussed by Gandhi and Williams.<sup>4,13</sup> Williams has developed a molecular model which expresses the polymer-solvent thermodynamic dependence of  $\eta_{sp0}$ .<sup>14</sup> The Williams model was empirically modified by Gandhi and Williams to predict the  $\eta_{sp0}$  curves for good solvent-polymer systems.<sup>4</sup>

In this paper we present data for the viscosity function of solutions of styrene-acrylonitrile (SAN) copolymers in several polar and nonpolar solvents and thermodynamic data for these systems. The behavior described in the preceding paragraph is observed. Several techniques for correlating solution viscosity with concentration are evaluated. The solution viscosity behavior is qualitatively related to the thermodynamics of the system through the Flory-Huggins interaction parameter for the solvent and polymer in solution.

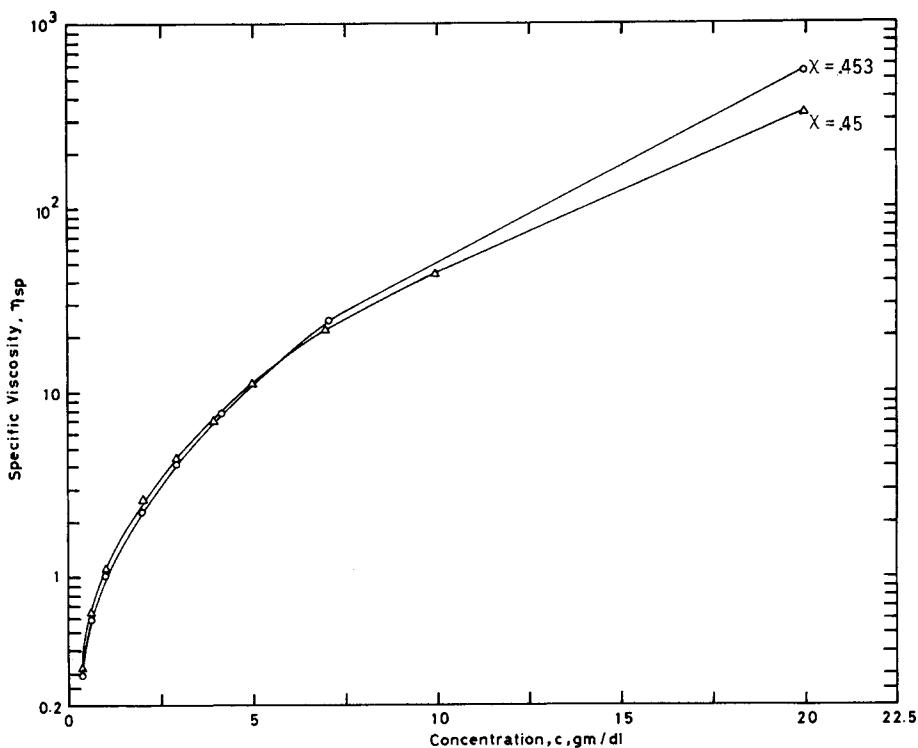


Fig. 1. Specific viscosity  $\eta_{sp}$  vs concentration  $c$  of SAN C-1 in ( $\Delta$ ) DMF and ( $\circ$ ) MEK at 30°C.

## EXPERIMENTAL

Four samples of SAN copolymers were prepared, each having different molecular weight and different acrylonitrile (ACN) content, thus different polarity. These samples were prepared in bulk at 60°C, utilizing  $\alpha, \alpha'$ -azobisisobutyronitrile as initiator. The monomers and initiator were purified using appropriate procedures.<sup>5</sup> Reactions were carried out, with agitation, to low conversions in order to minimize copolymer composition drift during copolymerization, and thus the samples prepared were of uniform composition. The uniformity of the chemical composition of the copolymer samples was indicated by the data from the light-scattering experiments which could be treated with equations describing homogeneous samples and which yielded data agreeing with GPC data. The copolymer samples were analyzed for nitrogen content (and thus ACN content), and for molecular weight and molecular weight distribution by gel permeation chromatography. Two samples of polystyrene homopolymer were also prepared. Table I describes the polymer and copolymer samples prepared for this investigation.

The properties of a particular linear homopolymer are determined primarily by two factors: average molecular weight and molecular weight distribution. In copolymers, along with the above two factors, two additionally important factors are the average chemical composition and the distribution of composition about this average. The copolymers synthesized in this work were similar to industrial polystyrene (PS) and SAN copolymers with respect to molecular

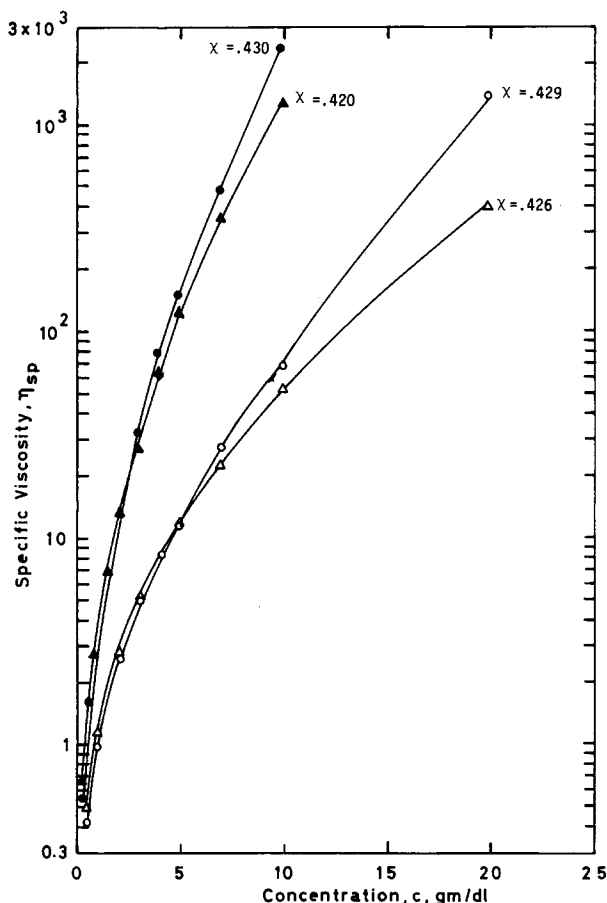


Fig. 2. Specific viscosity  $\eta_{sp}$  vs concentration  $c$  of (O) SAN C-2 and (●) SAN C-2' in (Δ) DMF and (○) MEK at 30°C.

weights and molecular weight distributions. Average chemical composition and molecular weight were variable for different samples studied; molecular weight distributions and composition distributions were essentially identical for all samples prepared.

Four solvents were selected for this work: (1) benzene, (2) dioxane, (3) methyl ethyl ketone (MEK), and (4) dimethylformamide (DMF). Benzene is nonpolar and is a good solvent for polystyrene (PS) while it is a nonsolvent for polyacrylonitrile (PAN). Dioxane has two symmetric oxygen atoms, and hence its dipole moment is zero, however, it does possess a local charge separation. Dioxane is a relatively good solvent for PS and a nonsolvent for PAN. The two polar solvents, MEK and DMF, are relatively poor solvents for PS, while for PAN MEK is a nonsolvent and DMF is a good solvent. This choice of solvents provides a wide range of polymer-solvent intermolecular interactions. The thermodynamic quality of each solvent for each polymer, or copolymer, was determined from light-scattering and intrinsic viscosity measurements. Light-scattering experiments were conducted using a Brice-Phoenix light scattering photometer of the series 2000 located in a low-humidity constant-temperature room. Details of these experiments are available elsewhere.<sup>5</sup> Twelve scattering angles and four

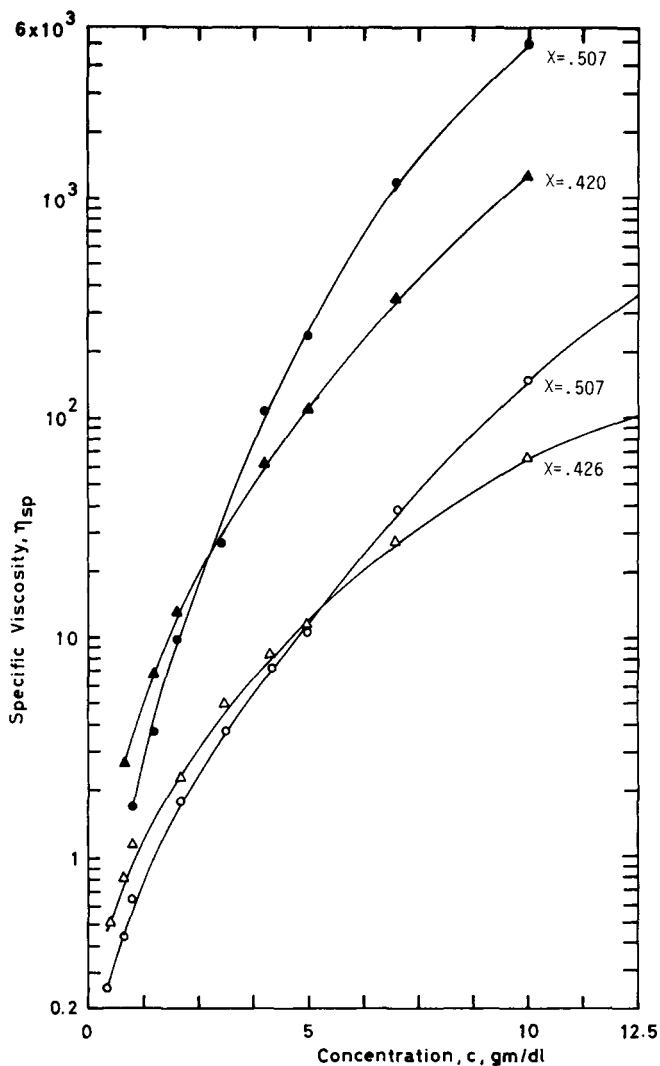


Fig. 3. Specific viscosity  $\eta_{sp}$  vs concentration  $c$  of (O) SAN C-2 and (●) SAN C-2' in (Δ) DMF and, (○) benzene at 30°C.

polymer solution concentrations were used for each system investigated in these experiments. Specific refractive index increments for each polymer-solvent pair were determined using a Brice-Phoenix differential refractometer Model BP-2000-V.

Intrinsic viscosities and dilute solution viscosities were measured in Cannon-Ubbelohde suspended level U-tube capillary viscometers of the four-bulb type for obtaining four different shear rates per sample. In this dilute concentration range the solution viscosities were independent of shear rate. Temperature of measurement was held constant by clamping the viscometers vertically in an insulated water bath equipped with a precision thermostat. Before introducing the solutions into the viscometers, they were filtered by pressure filtration through ultrafine sintered glass filters.

A cone-and-plate viscometer was used to measure the viscosities of the more

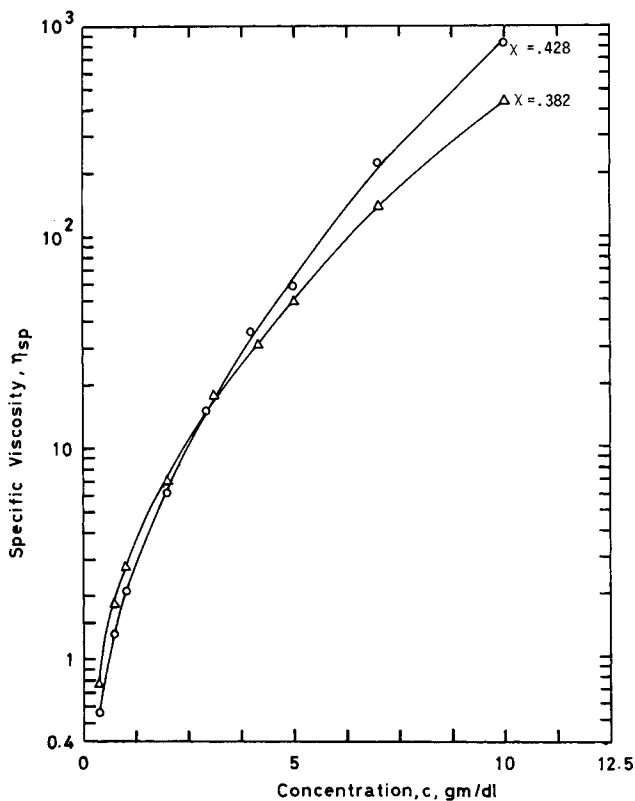


Fig. 4. Specific viscosity  $\eta_{sp}$  vs concentration  $c$  of SAN C-3 in ( $\Delta$ ) DMF and ( $\circ$ ) MEK at 30°C.

TABLE I  
Description of Polymer and Copolymer Samples

Polymer	Composition, wt-% styrene	$\frac{M_w \times 10^{-5}}{GPC^a}$		$M_n \times 10^{-5}$ GPC	$M_w/M_n$ GPC
		GPC <sup>a</sup>	L.S. <sup>a</sup>		
PS-1	100	1.85	1.91	1.03	1.79
PS-2	100	5.01	5.04	2.41	2.08
SAN C-1	85.8	2.75	2.90	1.41	1.95
SAN C-2	76.0	2.03	1.80	1.20	1.69
SAN C-2'	77.0	6.34	6.66	3.39	1.87
SAN C-3	62.0	3.32	3.32	2.05	1.62

<sup>a</sup> GPC = gel permeation chromatography, Dow Chemical Company Laboratories; L.S. = light scattering, Michigan State University Laboratories.

concentrated polymer solutions. A Weissenberg rheogoniometer Model R-16 was available for this purpose, with a platen diameter of 7.5 cm and a cone angle of 1°37'. Steady-state measurements were taken from the lowest to the highest shear rates attainable with this instrument, starting with low levels and increasing to the highest. Occasionally, readings were repeated back to the lowest value of shear rate starting with the highest. The viscosity curves could be essentially retraced from high speed to low speed. With several of the concentrated solutions non-Newtonian effects were observed. There were, however, enough data points at low shear rate to reliably determine the low-shear limit  $\eta_0$ . With the

solvents used in this study evaporation was severe. A specially designed reservoir chamber was used to minimize the effect of this upon the data obtained. The aluminum chamber was constructed to fit around the platens. This chamber and the gap between the platens were filled with test solution. The reservoir chamber was completely surrounded by a constant-temperature box. Viscosities between 0.1 and 0.5 poise were measured by both the capillary viscometers and the cone-and-plate viscometer. The experimental viscosities obtained by each of the two methods were within 5% of each other. This is within the error bounds of the cone-and-plate instrument.

## RESULTS AND DISCUSSION

### Thermodynamic Quality of a Solvent

The primary goal of this investigation was to examine the effect of polymer solution thermodynamics upon polymer solution viscosity. We choose to rank the thermodynamic quality of a solvent for a polymer (good solvent or poor solvent) based upon considerations of the Flory-Huggins equation,<sup>15-17</sup> the second virial coefficient from light-scattering, and intrinsic viscosity measurements. The Flory-Huggins equation gives the free energy of mixing of polymer (2) with solvent (1):

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi \phi_2 n_1 \quad (3)$$

In eq. (3),  $n_i$  is number of moles of component  $i$ ,  $\phi_i$  is volume fraction of component  $i$ , and  $\chi$  is the Flory-Huggins thermodynamic interaction parameter. In order for a given solvent to dissolve a polymer, the free energy of mixing should be negative. Since the first two terms in eq. (3) are always negative, this means the smaller the value of  $\chi$ , the interaction parameter, the better the thermodynamic quality of the solvent for the polymer.

Light scattering experiments and intrinsic viscosity measurements may be combined to measure the thermodynamic interaction parameter.<sup>18,19</sup> The second virial coefficient from light scattering,  $A_2$ , and the expansion factor  $\alpha$  yield the parameter  $\chi$  as shown in eqs. (4), (5), and (6):

$$A_2 = (\bar{v}_p^2/v_s)(1/2 - \chi) F(x) \quad (4)$$

$$x = 2(\alpha^2 - 1) \quad (5)$$

$$F(x) = 1 - \frac{x}{2!2^{3/2}} + \frac{x^2}{3!3^{3/2}} - \frac{x^3}{4!4^{3/2}} + \dots \quad (6)$$

where  $\bar{v}_p$  is the specific volume of the polymer and  $v_s$  is the molar volume of solvent. The expansion factor  $\alpha$  may be obtained as the cube root of the ratio of the intrinsic viscosity for the solution to the intrinsic viscosity in a  $\theta$  solvent.<sup>20,24</sup>

In a good solvent the interaction parameter for the solvent-polymer pair is less than the interaction parameter for a solvent-polymer pair in a poor solvent. In a good solvent the second virial coefficient, the expansion factor, and the intrinsic viscosity are greater than the corresponding properties in a poor solvent. These parameters are shown in Table II for the systems studied. The relative

TABLE II  
 Thermodynamic Parameters

Polymer	Solvent	$A_2 \times 10^4$ , mole cc/g <sup>2</sup>	$\chi$	$[\eta]$ , dl/g	$\alpha^a$
PS-1	benzene	5.64	0.426	0.782	1.278
	dioxane	4.83	0.443	0.622	1.184
	MEK	1.73	0.481	0.433	1.050
PS-2	benzene	5.71	0.424	1.619	1.380
	dioxane	—	—	1.503	1.346
	MEK	—	—	0.785	1.084
SAN C-1	dioxane	6.82	0.418	1.007	1.150
	benzene	5.36	0.433	0.988	1.143
	DMF	4.80	0.450	0.867	1.094
	MEK	4.00	0.453	0.783	1.058
SAN C-2	DMF	6.92	0.426	0.862	1.185
	dioxane	6.10	0.426	0.816	1.164
	MEK	5.70	0.429	0.742	1.128
	benzene	-0.66	0.507	0.446	0.952
SAN C-2'	DMF	6.76	0.420	2.110	1.287
	dioxane	6.00	0.426	1.987	1.261
	MEK	5.64	0.430	1.776	1.215
	benzene	-0.68	0.507	0.725	0.901
SAN C-3	DMF	10.10	0.382	1.653	1.218
	MEK	5.66	0.428	1.219	1.107
PAN	DMF	19.10 <sup>b</sup>	—	—	—

<sup>a</sup> Reference 22 was used for obtaining  $\eta_\theta$ .

<sup>b</sup> Reference 21.

thermodynamic quality of each solvent for each polymer is shown in Table II, which is arranged in order of descending quality of solvent.

### Low-Shear Viscosity Data

Solvent structure has an important influence on the value of low-shear specific viscosity of polymer solutions in both dilute and concentrated solutions. Viscometric data are shown in Figures 1–4. Data are also presented in Table III. At low concentrations,  $\eta_{sp0}$  is smaller in poor solvents than in good solvents for all of the systems investigated. As a general trend the viscosity of the solutions in a poor solvent tends to increase more rapidly than the viscosity in a good solvent so that, at moderate to high concentrations (10–20 g/dl), the solution specific viscosity is higher in poor solvents than in good solvents. This is true for all of the solvents for the 24% ACN and 38% ACN copolymer samples and for all of the polymers in the polar solvents DMF and MEK. For PS homopolymer in the solvent group benzene, dioxane, and MEK, the values of  $\eta_{sp0}$  in the good and poor solvents are approaching each other but have not yet become equal at a concentration of 20 g/dl. In the case of the 14% ACN copolymer the dioxane–benzene solvent pair and the DMF–MEK solvent pair exhibit specific viscosity crossover phenomena as concentration increases. However,  $\eta_{sp0}$  values in the four solvents do not exhibit order as they do in the higher ACN copolymer systems. The results for the PS–DMF solutions appear anomalous; perhaps the polymer was not truly dissolved in the solvent in this case.



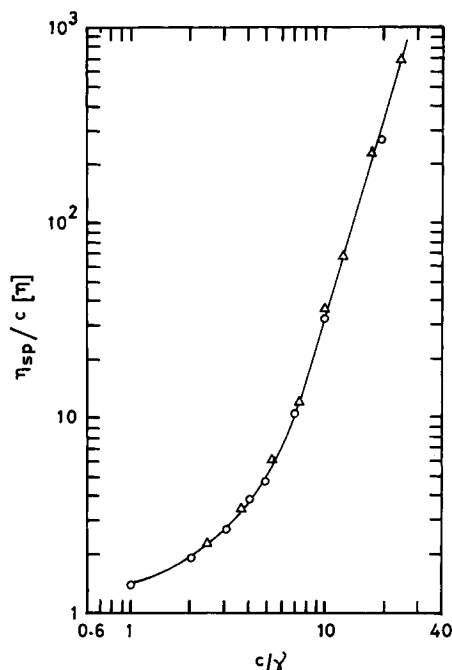


Fig. 5. Simha plot for (○) SAN C-2 and (Δ) SAN C-2' in benzene at 30°C.

The observation that for moderately concentrated solutions the specific viscosity of a polymer solution in poor solvents is significantly larger than the viscosity in good solvents was also made by Gandhi and Williams for PS-decalin-toluene and poly(methyl methacrylate)-chlorobenzene-xylene<sup>4</sup>; for PVC-acetate copolymer-cyclohexanone-MEK by Jansen and Caldwell<sup>23</sup>; for PS-decalin-ethylbenzene by Tager et al.<sup>12</sup>; and in PS solutions by Klein and Woernle.<sup>25</sup> It appears that polymer entanglement kinetics is influenced by polymer-solvent thermodynamics. It is possible in the poor solvent environment that the lifetime of entanglement junctions might be increased to the point of aggregation.

In comparing the data obtained in this work with data from the references cited in the previous paragraph for a particular polymer in a solvent pair, the crossover concentration (the concentration at which  $\eta_{sp0}$  values in good and poor solvents are equal) is much lower for SAN copolymer solutions than for PS homopolymer solutions. Gandhi and Williams<sup>4</sup> observed that the crossover concentration in the polar homopolymer poly(methyl methacrylate) systems was lower than in PS systems, and we find that it is still lower in the SAN copolymer systems. For SAN copolymer in the two solvents DMF and MEK, the crossover concentration decreases as ACN content of the copolymer increases. Gandhi and Williams<sup>4</sup> work indicated that the crossover concentration for the systems which they investigated was relatively insensitive to polymer molecular weight. Based upon our data for SAN C-2 and SAN C-2', it appears that the crossover concentration is lower in the case of the higher molecular weight copolymer.

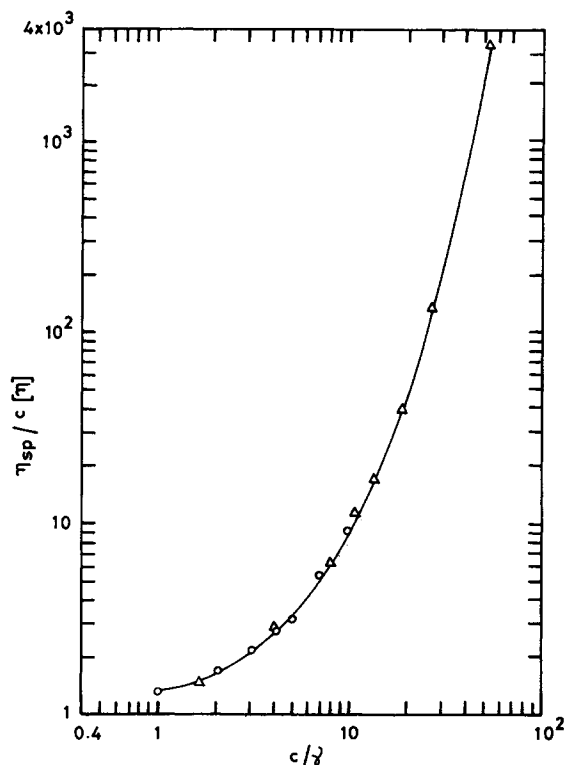


Fig. 6. Simha plot for (O) SAN C-2 and ( $\Delta$ ) SAN C-2' in MEK at 30°C.

### Data Correlation

Three available techniques were used to examine the data obtained in this work: a corresponding states relationship of Simha and Utracki<sup>26</sup>; several characteristic entanglement network correlations<sup>10,27,28</sup>; and a molecular model of Gandhi and Williams.<sup>4</sup> In the Simha and Utracki method, log-log plots of the group  $\eta_{sp0}/c[\eta]$  versus  $c/\gamma$  are prepared for different molecular weight polymers in a common solvent. Then  $\gamma(M)$  is chosen as a shift factor such that these plots merge into a single master plot. This correlation was tested here for solutions of SAN C-2 and SAN C-2' copolymers in four solvents up to moderately high concentration. Correlations were successful for the SAN copolymers in benzene and DMF solvents for values of  $\eta_{sp0}/c[\eta]$  up to 500, corresponding to a copolymer concentration in solution of about 10 g/dl. For the solvents dioxane and MEK the correlations were useful up to values of  $\eta_{sp0}/c[\eta]$  of 10–50, corresponding to concentrations of 6–8 g/dl. Plots are shown in Figures 5–8. Simha and Utracki reported the factor  $\gamma$  to be proportional to  $M^{-a_1}$ , with  $0.47 \leq a_1 \leq 1.1$ ,  $a_1$  being larger for good than for poor solvents.<sup>26</sup> Based on the two samples C-2 and C-2', this proportionality holds with values of  $a_1$  being 0.75 in benzene and dioxane, 0.81 in MEK, and 0.84 in DMF. Although this correlation scheme appears to be satisfactory, the parameter  $\gamma$  is not predictable from thermodynamic measurements alone.

Features of the viscometric data may also be examined from log-log plots of the viscosity-concentration data. For this purpose  $\eta_{sp0}$  or  $\eta_{r0}$  may be used. Such curves often show an abrupt increase in slope at a concentration characteristic

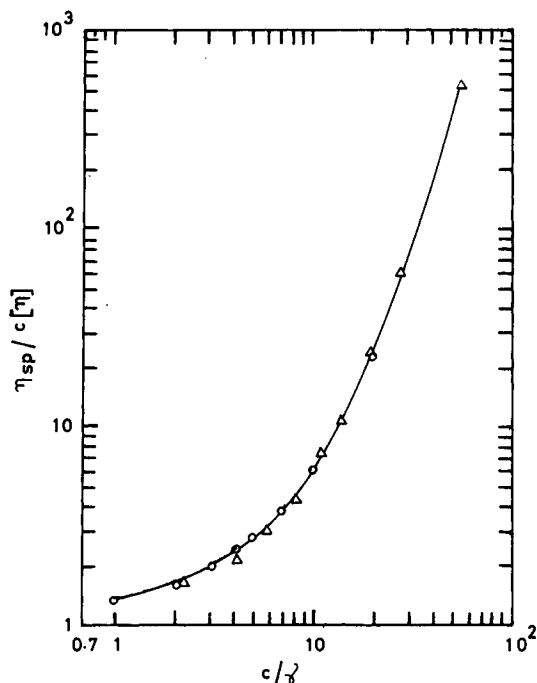


Fig. 7. Simha plot for (O) SAN C-2 and( $\Delta$ ) SAN C-2' in DMF at 30°C.

of entanglement network formation. The onset of entanglement phenomena in polymer solutions may be observable from plots of  $\eta_{r0}$  versus  $c$  or  $cM^b$  or from plots of  $\eta_0$  for polymer melts versus  $M$ . In the latter case the molecular weight of the polymer at the onset of entanglement manifestation is termed  $M_c$ . For polymer solutions, Porter and Johnson<sup>10</sup> recommend

$$c_{\text{ent}}M = \rho M_c \quad (7)$$

where  $\rho$  is bulk polymer density and  $c_{\text{ent}}$  is the entanglement concentration in solution for a polymer of molecular weight  $M$ . Cornet<sup>27</sup> and Onogi<sup>28</sup> have proposed

$$c_{\text{ent}}M^{1/2} = \text{constant} \quad (8)$$

or

$$(c/M)_{\text{ent}} = 2.28 \times 10^{-23} / \langle l_0^2 \rangle^{3/2} \quad (9)$$

where  $\langle l_0^2 \rangle$  is the mean square end-to-end distance of a polymer chain in the unperturbed state. None of the above relations includes information about the solvent component in the solution. For PS three values of  $M_c$  and one value of the constant in eq. (8) were found in the literature. No values for SAN copolymer were found. Table IV lists values for  $c_{\text{ent}}$  for the polymers and copolymers obtained in this work, and Figures 9 and 10 show representative behavior. The curves are relatively smooth, showing no abrupt discontinuities. However, the slope is increasing rapidly near the concentration indicated on the figures.

Based upon Table IV, the correlation in line 1 of the table seems preferable for PS. The solvent significantly influences the value of  $c_{\text{ent}}$ . Equation (9) yields reasonable estimates of  $c_{\text{ent}}$  for the copolymers in good solvents. The correlation

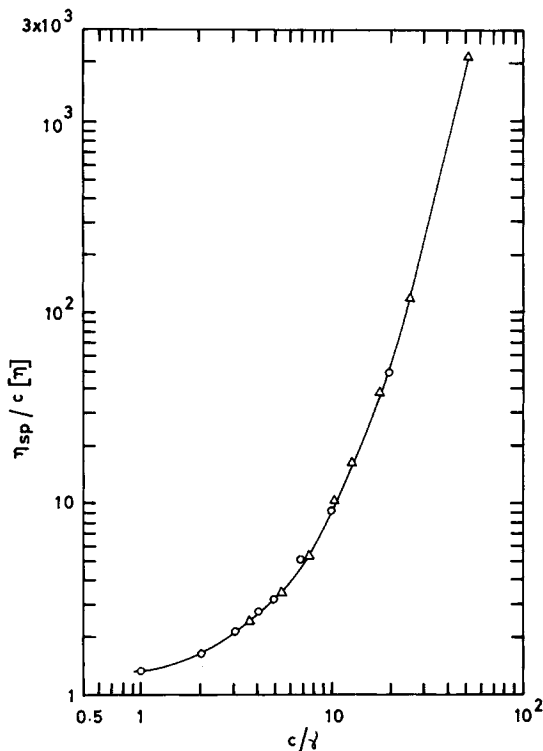


Fig. 8. Simha plot for (O) SAN C-2 and ( $\Delta$ ) SAN C-2' in dioxane at 30°C.

$(cM)_{\text{ent}} = \text{constant}$  was not attempted for the SAN samples in Table IV because of the absence of melt data or other data for entanglements in the SAN system. In poor solvents the observed values of  $c_{\text{ent}}$  are less than predicted by eq. (9). These observations are consistent with those of Gandhi and Williams.<sup>13</sup> Most published relations for predicting  $c_{\text{ent}}$  are based upon measurements in good solvents. The influence of the solvent on entanglement concentration was therefore not observed. Published correlations for entanglement concentrations may not be useful for solutions of polymers in poor solvents.

An empirical fit of the data was obtained using eq. (2). Representative log-log plots of  $\eta_{r0}$  versus  $cM^b$  are shown in Figures 11 and 12. The function  $\eta(cM^b)^\beta$  provides a reasonable fit to the data in DMF, a good solvent, with the value of  $b = 0.68$ . A value of  $b = 0.625$  is a better representation for the data in the poor solvent, benzene. A value of 0.625 is predicted by a theory of Williams.<sup>14</sup> Gandhi and Williams found that a value of  $b$  for the PS-decalin system, with decalin a near theta solvent, was 0.5.<sup>4</sup> For one particular polymer in different solvents correlations using a single value of the exponent  $b$  may not be possible unless all solvents under consideration are good solvents.

Williams has developed a molecular theory which may be used to describe the low-shear viscosity of moderately concentrated polymer solutions.<sup>14</sup> This theory utilizes Fixman's description of stresses in solutions of linear polymers, with the solvent represented as a continuum phase creating frictional resistance to flow in a solution of polymer molecules composed of links and segments.<sup>31</sup> The resulting equation is

$$\eta_{r0} = 1 + [\eta]c + \left(\frac{cN_{AV}}{M}\right)^2 \left(\frac{A}{kT}\right) \frac{B^{3/2}(C\xi)}{\eta_s} \quad (10)$$

TABLE III  
Low-Shear Viscosities, 30°C<sup>a</sup>

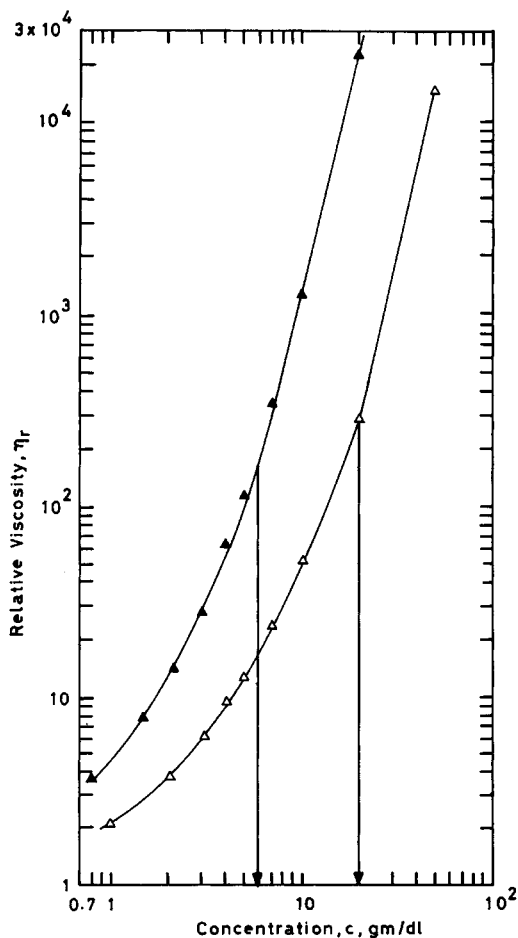
Polymer	Solvent	$\eta_0$ , centipoises			$\eta_{sp}$				
		1 g/dl <sup>b</sup>	2	10	20	10	20	35	
PS-1	benzene	1.128	1.768	22.65	110.0	1.006	2.145	39.29	194.7
	dioxane	1.941	3.087	—	190.0	0.7854	1.84	—	173.8
	DMF	1.162	—	—	70.0	0.5253	—	—	90.9
PS-2	MEK	0.502	0.749	7.62	65.0	0.3763	1.053	19.88	177.0
	benzene	2.576	4.827	185.0	3100	3.5835	7.588	328.1	5514
	dioxane	3.608	7.227	241.0	3299	2.319	5.649	220.7	3034.9
	DMF	—	—	78.0	1020	—	—	101.36	1337.6
SAN C-1	MEK	1.049	1.522	68.0	1070	1.8735	3.1699	185.3	2930.5
	dioxane	2.575	4.800	74.0	685	1.369	3.416	67.1	629.2
	benzene	1.226	2.319	48.0	680	1.1805	3.126	84.4	1208.8
	DMF	1.634	2.807	35.0	255	1.144	2.684	44.9	333.7
SAN C-2	MEK	0.752	1.202	—	200	1.0596	2.294	—	547
	DMF	1.622	2.906	41.0	300	1.129	2.813	52.8	392.7
	dioxane	2.259	4.152	83.0	870	1.0785	2.82	75.4	799.3
	MEK	0.722	1.314	25.0	500	0.979	2.6	67.5	1368.9
SAN C-2'	benzene	0.92	1.575	84.88	1369	0.6387	1.8015	150	2436.3
	DMF	2.833	6.041	980	17,200	2.719	6.928	1285.1	22571.2
	dioxane	—	9.486	2580	93,000	—	7.267	2372.5	85555.6
	MEK	0.955	3.198	861.6	40,000	1.617	7.762	2360.6	109,588
SAN C-3	benzene	—	2.687	2870	155,000	—	3.78	5105	275,752
	DMF	2.877	6.044	340	5,300	2.7752	6.9315	445.2	6954.4
	MEK	1.137	2.795	307	10,500	2.115	6.658	840.1	28,766

<sup>a</sup> Solvent  $\eta$  (centipoises, 30°C): benzene, 0.5621; dioxane, 1.087; DMF, 0.762; MEK, 0.365.

<sup>b</sup> Polymer concentration.

TABLE IV  
 Entanglement Concentrations

Polymer	Reference for equation	Literature		This work,	
		Equation	$c_{ent}$ calculated, g/dl	$c_{ent}$ measured, g/dl	Benzene
PS-1	10	$(cm)_{ent} = 4.41 \times 10^6$	23.8	>20	>20
	10	$(cm)_{ent} = 3.75 \times 10^6$	20.2	—	—
	29	$(cm)_{ent} = 3.03 \times 10^6$	16.4	—	—
	10	$(cm^{1/2})_{ent} = 5.20 \times 10^3$	12.3	—	—
	30	eq. (9)	10.9	—	—
PS-2	10	$(cm)_{ent} = 4.41 \times 10^6$	8.80	10	7
	10	$(cm)_{ent} = 3.75 \times 10^6$	7.5	—	—
	29	$(cm)_{ent} = 3.03 \times 10^6$	6.1	—	—
	10	$(cm^{1/2})_{ent} = 5.20 \times 10^3$	7.5	—	—
	30	eq. (9)	6.6	—	—
SAN C-2	22	eq. (9)	11.0	Benzene	DMF
SAN C-2'	22	eq. (9)	5.8	5	20
SAN C-3	22	eq. (9)	9.0	3	6
				5	10


 Fig. 9. Relative viscosity  $\eta_r$  vs concentration  $c$  of ( $\Delta$ ) SAN C-2 and ( $\blacktriangle$ ) SAN C-2' in DMF at 30°C.

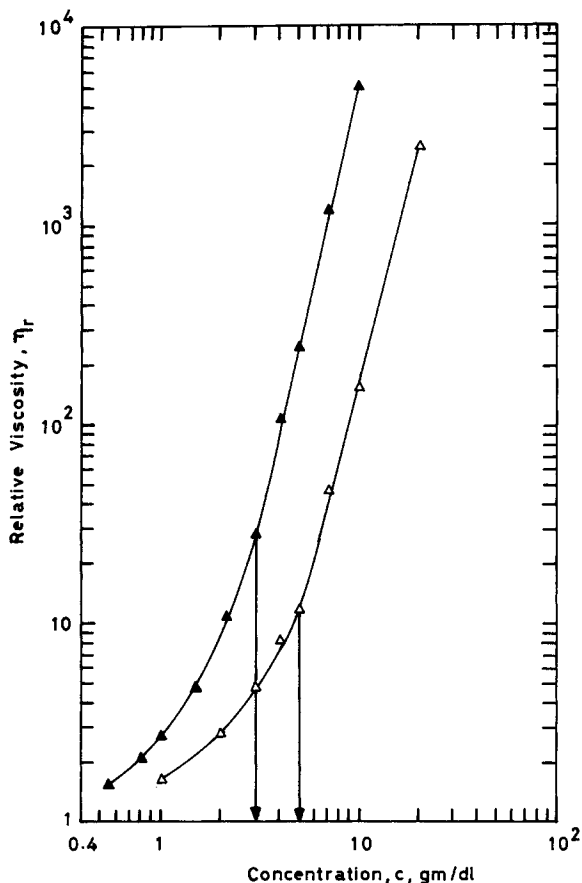


Fig. 10. Relative viscosity  $\eta_r$  vs concentration  $c$  of ( $\Delta$ ) SAN C-2 and ( $\blacktriangle$ ) SAN C-2' in benzene at 30°C.

The terms in eq. (10) are defined in the nomenclature section. This equation contains polymer concentration and molecular weight dependence explicitly. The parameter  $B$  also depends upon polymer molecular weight through the radius of gyration as shown below in eq. (12). The parameter  $A$  is a polymer-solvent thermodynamic term, eq. (11). Hydrodynamic or frictional resistance to flow is related to the parameter  $\xi$ .

Gandhi and Williams describe the use of eq. (10) in treating data obtained for solutions of PS and poly(methyl methacrylate).<sup>4</sup> In their work the thermodynamic parameter  $A$  was obtained from a modified Flory-Huggins equation with data from osmotic pressure measurements. In this work  $A$  was obtained from the second virial coefficient from light scattering using intrinsic viscosity and the expansion factor  $\alpha$ , eqs. (4) through (6):

$$\frac{A}{kT} = \frac{V_p^2}{V_s} \left[ \frac{1}{1 - \phi_p} - 2\chi \right] \quad (11)$$

where  $V_p$  is the molecular volume of a polymer molecule and  $V_s$  is the solvent molecular volume. Values of the interaction parameter  $\chi$  are listed in Table II. Williams' parameter  $B$  is obtained from the polymer radius of gyration at theta

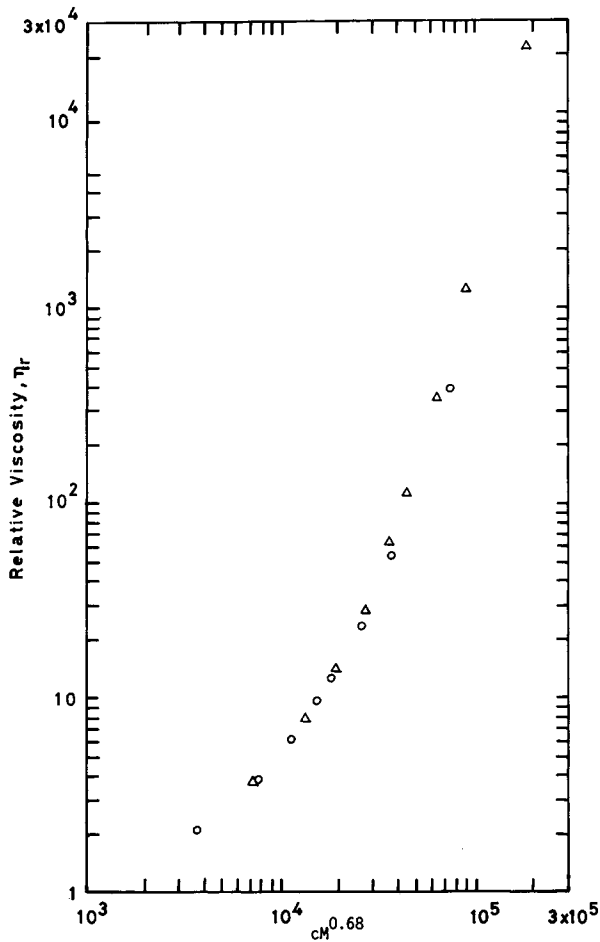


Fig. 11. Relative viscosity  $\eta_r$  vs  $cM^{0.68}$  for (O) SAN C-2 and ( $\Delta$ ) SAN C-2' in DMF at 30°C. conditions,  $\langle s_0^2 \rangle^{1/2}$ :

$$B = (4\langle s_0^2 \rangle)^{-1} \quad (12)$$

The parameter  $C$  in eq. (10) is obtained from  $A$  and  $B$ :

$$C = \frac{1}{30(2\pi)^{1/2}} \left[ \frac{3.53}{2B \ln \left( \frac{N_{AV} C A}{M kT} \right)^{1/2}} \right]^5 \quad (13)$$

For evaluation of  $\xi$  the original theory of Williams was based upon Kirkwood's treatment of the friction coefficient in polymer solutions.<sup>32</sup> The use of eq. (10) with  $\xi$  from Kirkwood's theory resulted in values for  $\eta_0$  that were far too low for polymer-solvent systems considered in this work<sup>5</sup> and in the work of Gandhi and Williams.<sup>4</sup> Gandhi and Williams suggested, therefore, the use of a hydrodynamic friction coefficient  $\xi'$ , based upon Frankel and Acrivos' derivation for frictional effects in concentrated solutions of uniform solid spheres<sup>33</sup>:

$$\xi' = 3\pi\eta_0 \langle s_0^2 \rangle / (M/cN_{AV})^{1/3} \quad (14)$$



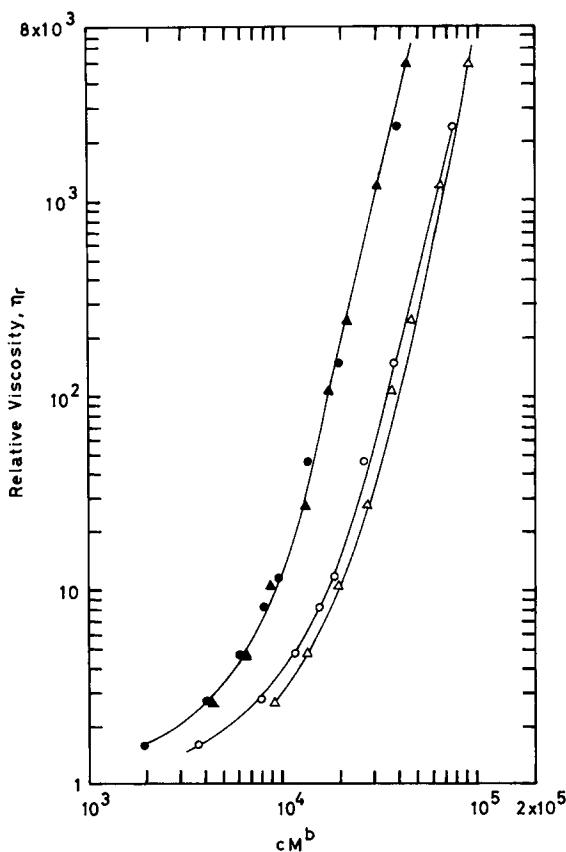


Fig. 12. Relative viscosity  $\eta_r$  vs  $cM^b$  for (O) SAN C-2 and ( $\Delta$ ) SAN C-2' in benzene at 30°: (O) and ( $\Delta$ )  $b = 0.68$ ; (●) and ( $\blacktriangle$ )  $b = 0.625$ .

Figures 13 and 14 show typical results comparing calculations of relative viscosity  $\eta_{r0}$  from eq. (10) with the experimental data obtained in this work. Up to moderate concentrations, agreement between the Williams equation and the experimental data is of the correct order of magnitude in good solvents, and the curves of predicted and experimental viscosities are roughly parallel at moderate concentrations. Agreement is not good at higher concentrations where entanglements, aggregations, and three-body interactions render Williams' theoretical treatment invalid. The concentrations where disagreement becomes substantial depend upon polymer molecular weight and are lower for higher molecular weights. Calculations in poor solvents do not agree qualitatively with data; and theta conditions,  $A_2 = 0$ , or conditions of negative  $A_2$ , such as those in benzene, lead to mathematical problems at low concentrations where  $A/kT$  is negative and  $C$  is undefined, or to poor predictions at higher concentrations. It was also pointed out in reference 4 that eq. (14) is especially inadequate with poor solvents. It should be noted that in their work Gandhi and Williams used a concentration-dependent thermodynamic parameter, whereas the interaction parameter  $\chi$  used in this paper was a constant,  $\chi_0$  in reference 4. The similarity between our data fit and the work reported in reference 4 appears to indicate that this does not create major inaccuracies. However, including the concentration de-

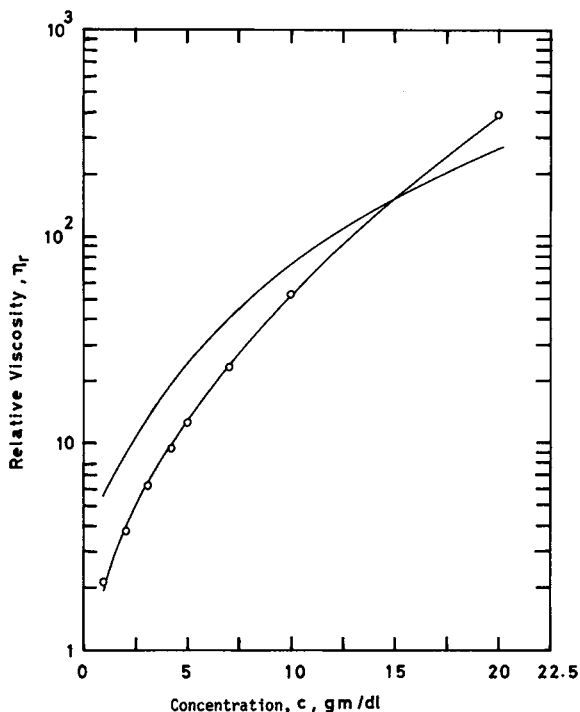


Fig. 13. Experimental and calculated relative viscosity  $\eta_r$  vs concentration  $c$  of SAN C-2 in DMF at 30°C: (—) theoretical; (—O—O—) experimental.

pendence of thermodynamic parameters when fitting the concentration dependence of viscosity would be the preferred procedure when such data is available.

### CONCLUSIONS

The principle conclusion to be drawn, or perhaps reemphasized, is that the thermodynamic interaction between a solvent and a polymer in solution influences the rheological behavior of the system. At low concentrations of polymer in solvent, the low-shear solution viscosity is larger in a good solvent than in a poor solvent. In solutions of higher polymer concentration, low-shear solution viscosity may be significantly larger in a poor solvent than in a good solvent. The solvent structure has a significant influence on viscosity over the whole range of polymer concentrations. This result is not predicted quantitatively by existing theory nor accounted for in correlation schemes presently in use.

The concentration at which the specific low-shear viscosities of one polymer in good and poor solvents are equal, the "crossover" concentration, is much lower for the highly polar SAN copolymer solutions than for PS or poly(methyl methacrylate) homopolymer solutions and is therefore apparently lower for polar polymers than for nonpolar polymers. The crossover point may be a function of molecular weight.

Widely used viscosity correlation techniques, such as the power law, or Simha correlation, do not quantitatively include solvent effects *a priori*. While such techniques may correlate data for a polymer or polymer family in one solvent

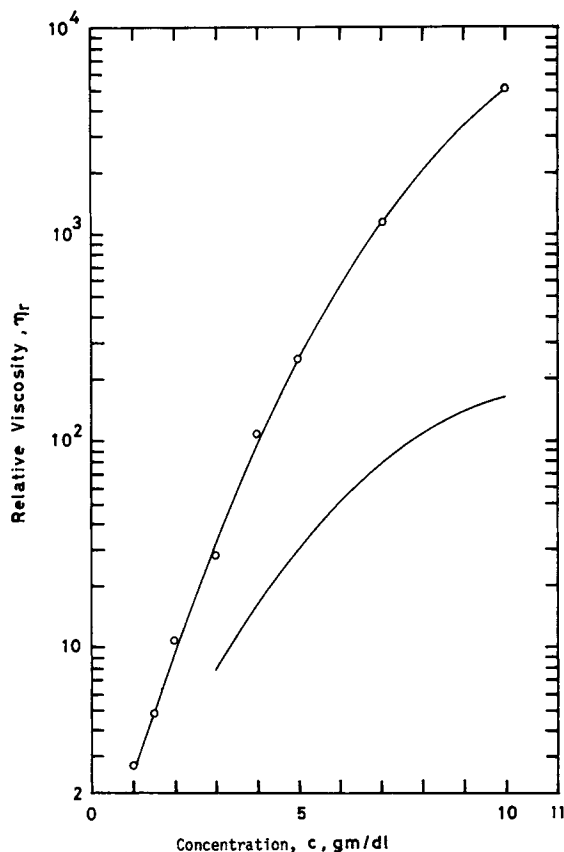


Fig. 14. Experimental and calculated relative viscosity  $\eta_r$  vs concentration  $c$  of SAN C-2 in benzene at 30°C: (—) theoretical; (—O—O—) experimental.

or in solvents of similar thermodynamic nature, the parameters in the correlations are solvent dependent. Likewise, entanglement concentrations in polymer solutions depend upon the solvent environment present. There appears to be a direct relationship between the entanglement concentration for a particular polymer in various solvents and the expansion factor  $\alpha$  for a polymer-solvent pair. The lower the value of  $\alpha$ , the lower the value of  $c_{ent}$ .

A molecular model of Williams<sup>14</sup> as modified by Gandhi and Williams,<sup>4</sup> which describes the viscosity of polymer solutions and which includes the free energy of mixing polymer with solvent, can give order-of-magnitude estimates of low-shear viscosity at moderate concentrations for solutions in good solvents. The model is not valid at higher concentrations nor for solutions in poor solvents.

### Nomenclature

- $a$  exponent, eq. (1), empirical relationship between intrinsic viscosity and polymer molecular weight
- $A$  thermodynamic function of intermolecular potential energy, g cm<sup>5</sup>/sec<sup>2</sup>, eqs. (10) and (11)
- $A_2$  coefficient in the virial expansion, mole cm<sup>3</sup>/g<sup>2</sup>

$b$	exponent in power law correlations of viscosity, eq. (2)
$B$	factor related to molecular size, $\text{cm}^{-2}$ , eqs. (10) and (12)
$c$	concentration, g/dl
$c_{\text{ent}}$	entanglement concentration, eqs. (7) and (8)
$C$	parameter in the Williams equation, eqs. (10) and (13)
$\Delta G_m$	Gibbs free-energy change on mixing
$k$	Boltzman's constant
$K$	constant in the intrinsic viscosity-molecular weight relation, eq. (1)
$\langle l^2 \rangle$	mean square end-to-end distance of a polymer chain in any and in
$\langle l_0^2 \rangle$	unperturbed states, respectively
$m$	ratio of molar volumes, polymer to solvent
$M$	polymer molecular weight
$M_c$	critical molecular weight, eq. (7)
$n$	number of moles
$N_{\text{AV}}$	Avogadro's number
$R$	gas constant
$\langle s^2 \rangle$	mean square radius of gyration of a polymer molecule in any and in
$\langle s_0^2 \rangle$	unperturbed states, respectively
$T$	absolute temperature
$v_s$	solvent molar volume
$V_s$	solvent molecular volume
$v_p$	polymer specific volume
$V_p$	polymer molecular volume
$x$	parameter in eqs. (4), (5), and (6)
$\alpha$	polymer expansion factor
$\beta$	power law correlation exponent in eq. (2)
$\gamma$	Simha correlation parameter
$\dot{\gamma}$	shear rate, $\text{sec}^{-1}$
$\eta, \eta_0$	non-Newtonian viscosity function at any and low shear rates, respectively
$\eta_r$	relative viscosity $\eta/\eta_s$
$\eta_s$	solvent viscosity
$\eta_{sp}$	specific viscosity
$[\eta]$	intrinsic viscosity
$\mu$	Newtonian viscosity
$\xi, \xi'$	friction coefficient in Williams' model, eqs. (10) and (14)
$\tau$	shear stress
$\phi$	volume fraction
$\chi$	Flory-Huggins thermodynamic interaction parameter

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### References

1. G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, **5**, 261 (1968).
2. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, Chap. 17.

3. S. Middleman, *The Flow of High Polymers*, Interscience, New York, 1968, Chap. 5.
4. K. S. Gandhi and M. C. Williams, *J. Polym. Sci. C*, **35**, 211 (1971).
5. B. N. Shah, Thesis, Michigan State University, Department of Chemical Engineering, May 1975.
6. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, Chap. 9.
7. S. Middleman, *The Flow of High Polymers*, Interscience, New York, 1968, Chap. 4.
8. H. Morawetz, *Macromolecules in Solution*, Interscience, New York, 1966, Chap. 6.
9. S. Middleman, *The Flow of High Polymers*, Interscience, New York, 1968, Chap. 5, pp. 171 and 172.
10. R. S. Porter and J. F. Johnson, *Chem. Rev.*, **66**, 1 (1966); R. S. Porter, W. J. MacKnight, and J. F. Johnson, *Rubber Chem. Technol.*, **41**, 1 (1963).
11. J. D. Ferry, *Viscoelastic Properties of Polymers*, 2nd ed., Wiley, New York, 1970, Chap. 17, p. 544.
12. A. A. Tager, et al., *J. Polym. Sci.* **6**, **23**, 181 (1968).
13. K. S. Gandhi and M. C. Williams, *J. Appl. Polym. Sci.*, **16**, 2721 (1972).
14. M. C. Williams, *A.I.Ch.E. J.*, **12**, 1064 (1966); *ibid.*, **13**, 534 (1967).
15. J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, Englewood Cliffs, New Jersey, 1969, p. 294.
16. M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **41**, 1 (1942); P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
17. P. J. Flory, *Disc. Faraday Soc.*, **49**, 7 (1970).
18. H. Morawetz, *Macromolecules in Solution*, Interscience, New York, 1966, Chap. 6, pp. 246-248.
19. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Chap. 12.
20. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953, Chap. 12, p. 612.
21. W. R. Krigbaum and A. M. Kotliar, *J. Polym. Sci.*, **32**, 323 (1958).
22. Y. Shimura, *J. Polym. Sci. A*, **4**, 423 (1966).
23. A. G. Jansen and B. P. Caldwell, *Polym. Bull.*, **1**, 120 (1945).
24. H. Tompa, *Polymer Solutions*, Butterworth, London, 1956, Chap. 9.
25. J. Klein and R. Woernle, *Kolloid-Z. Z. Polym.*, **237**, 209 (1970).
26. R. Simha and L. Utracki, *J. Polym. Sci., Part 2*, **5**, 853 (1967).
27. C. F. Cornet, *Polymer*, **6**, 373 (1965).
28. S. Onogi, et al., *J. Appl. Polym. Sci.*, **7**, 847 (1963).
29. D. Gupta and W. C. Forsman, *Macromolecules*, **2**, 304 (1969).
30. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Interscience, New York, 1966, Chap. 4.
31. M. Fixman, *J. Chem. Phys.*, **42**, 3831 (1965).
32. J. G. Kirkwood, *J. Chem. Phys.*, **14**, 180 (1946).
33. N. A. Frankel and A. Acrivos, *Chem. Eng. Sci.*, **22**, 847 (1967).

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