NOTES

Rapid Method for Determining Some Solution Viscosity Parameters

The intrinsic viscosity $[\eta]$ of polymer solutions is generally expressed by an equation due to Huggins[1]

$$\eta_{sp}/c = [\eta] + k[\eta^2]c \qquad (1)$$

where $\eta_{sp}[= (\eta - \eta_0)/\eta_0]$ is the specific solution viscosity, η_0 is the reference solvent viscosity, c is the solute concentration (g./dl.), and k is the Huggins constant. In order to obtain values of $[\eta]$ it is necessary to extrapolate viscosity data at finite concentrations to infinite dilution. The extrapolation method indicated by eq. (1) is most frequently used although a number of alternative graphical representations of experimental results can be employed.[2] In all such cases a relatively large number of experimental points is desirable. This accounts for a considerable time expenditure in routine determinations of $[\eta]$. The commonly used extrapolation suggested by eq. (1) has the further disadvantage of preferentially weighting data at low values of c. Since many viscosity determinations are performed by methods of successive dilution in the viscometer, these low concentration results are often subject to appreciably larger experimental errors than data at higher concentrations.

The tedium of multi-point experimental programmes can be reduced by using single-point methods for $[\eta]$ determination.[3,4] These commonly assume the existence of an invariant k value in eq. (1), thus permitting solution of the quadratic. Since k depends on solvent-solute interactions, the use of such single-point determinations can be formally justified only in solutions of homologous series of polymers in given solvents, preferably at a particular temperature and solute concentration.[1] The faster methods are therefore rather inflexible, and by their nature make an evaluation of the true value of k impossible. This is often undesirable because, as McCormick has recently shown,[5] interesting and potentially valuable correlations between k and solute structure may be possible.

The problem of avoiding a preferential weighting of less accurate experimental data in $[\eta]$ evaluations has been considered by Jungnickel and Weiss.[6] These authors write the viscosity equation as

$$\eta_{sp} = [\eta]c + bc^2 \qquad (2)$$

and use computational methods to evaluate $[\eta]$ and the Huggins constant from

$$k = b[\eta]^{-2} \qquad (3^*)$$

The method weights equally all experimental data and avoids the subjectivity of graphical analyses, but it assumes the availability of a computing device and in fact does not reduce the tedium of experimental work. Clearly, there is still a need for an experimental method which rivals the speed of single-point methods of evaluating $[\eta]$ and yet

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* The corresponding equation in ref. 6 is incorrectly stated as $k = b[\eta]$.[2]

retains sufficient flexibility to also evaluate the Huggins constant and to be widely applicable to polymer-solvent systems. We describe a two-point method intended to answer this need.

The Two-Point Method

If eq. (2) is an adequate representation of the relationship between η_{sp} and c, then eqs. (2) and (3) can be readily solved for $[\eta]$ and k, provided two accurately determined specific viscosities $(\eta_{sp})_1$ and $(\eta_{sp})_2$, corresponding to solute concentrations c_1 and c_2 $(c_2 > c_1)$, are known. Such a two-point determination would constitute a marked saving in experimental time over conventional multi-point methods, at the same time avoiding the need for computer data processing or subjective graphical analyses. The accuracy of the calculated results will depend largely on the accuracy of the primary data and on suitable selection of concentration values at which to determine the required specific viscosities. In this respect if, for simplicity, errors in measuring c_1 and c_2 are taken as additional errors in the corresponding specific viscosities, then it is readily shown that the errors in $[\eta]$ and b (and therefore k) are reduced as much as possible when the difference in solute concentrations $(c_2 - c_1)$ is made as large as possible. The two-point method of evaluating $[\eta]$ and k should therefore be based on experimental data using solute concentrations which are as widely separated as practical considerations allow. That is, the lower (c_1) values should not be so low as to lead to possible difficulties due to changes in effective capillary diameter.[7] The upper (c_2) value, on the other hand, should not lead to impractically long flow times and should avoid possible significant effects of higher power terms in c and $[\eta]$ in a fuller expansion of eq. (2). The concentration limits therefore will be characteristic of the chosen polymer-solvent system and may be defined by a suitable multi-point calibration experiment.

Experimental

The two-point method was tested in a number of polyolefin solution systems by comparing calculated $[\eta]$ and k values with data obtained by the more laborious multipoint techniques. Polymers included high pressure (HPPE) and low pressure (LPPE) polyethylenes, the latter both in fractionated and unfractionated form, ethylene-butene copolymers (EBC), and polypropylenes (PP). Solvents were α-chloronaphthalene (I), tetralin (II), α-methyl naphthalene (III), and decalin (IV). Fisher Scientific reagent grade samples of I and II were fractionally distilled, while reagent grade III and IV were used as received.

All viscosity measurements were carried out in modified Ubbelohde viscometers.[8] At least five experimental points were obtained by successive dilution within the viscometer. Flow times were measured to within 0.1 sec. at solute concentrations which varied from case to case but were always within the limits $0.08 < c < 0.70$ g./dl. Measurements were carried out at various temperatures in the range 120–140°C., controlled to ±0.07°C. in each case.

In graphical evaluations of $[\eta]$ and k, plots of η_{sp}/c vs. c and $\ln \eta_r/c$ vs. c (where $\eta_r = \eta/\eta_0$) were constructed and

a double extrapolation used to determine $[\eta]$. The same experimental data were used to compute $[\eta]$ and k from a least squares fitting to eq. (2), using the Bendix G-15D computer. The program weighted all experimental points equally. Finally, values of $[\eta]$ and k were calculated from simultaneous solutions of eqs. (2) and (3) using experimental data taken from near the limits of the studied concentration range, i.e., with $c_1 < 0.20$ and $c_2 > 0.50$ g./dl. In all cases these concentrations were chosen so as to comply with the conditions noted above. In a number of cases a second set of calculations was done with data in the narrow range $0.20 < c < 0.30$, to indicate the magnitude of errors incurred when the position of the assumed parabolic function of eq. (2) was defined over only a narrow range of the coordinates.

Results and Discussion

Intrinsic viscosities and Huggins constants for various polymer-solvent systems are compared in Table I. Values obtained from graphical and computer analyses of multi-point results are listed under corresponding headings in Table I. Very close agreement exists in every case between the graphical $[\eta]$ values and those computed from simul-taneous solutions of eq. (2) using solute concentrations near the limits of the range considered ("broad" form, Table I). On the other hand, use of solute concentrations in the range 0.2 to 0.3 g./dl. ("narrow" form, Table I), does not consistently result in $[\eta]$ values which are compatible with the former two techniques of evaluation, but can lead to quite serious, random deviations from these values (e.g., systems 2, 3, 5, 7). Ranodm deviations of this type would be expected if the position of the η_{ps} vs. c relationship were inadequately defined in its coordinates. Data from computer least-squares fitting of results are in most cases in good agreement with the conventional graphical and the "broad" two-point results, but in some cases (e.g., systems 4, 5) deviate appreciably from these. This is due to the inability of the present computer program to detect obviously unsatisfactory points. The selectivity of the computer program could, of course, be much improved but only at the cost of additional time and labor which would be contrary to the aims of the present research.

Inspection of the columns of Huggins constants again shows that graphical, computer derived, and calculated two-point values are generally in very satisfactory accord. Only the "broad" two-point evaluation of $[\eta]$ was used to calculate k values from eq. (3), the chosen solute concentra-

TABLE I
Comparison of Viscosity Parameters from Various Methods of Calculation

| System | | $[\eta]$, dl./g. | | | | k | | |
| | | Multi-point form | | 2 point form | | | | |
No.	Description	Graphical analysis	Computer analysis	broad	narrow	Graphical analysis	Computer analysis	2 point form
1	LPPE 1-I,[a] 120°C.	1.38	1.35_6	1.39_7	1.42	0.90	0.98	0.87
2	LPPE 2-II, 140°C.	1.88	1.81_5	1.83_9	1.61	0.52	0.53	0.54
3	LPPE 1F-II, 120°C.	0.53	0.52_7	0.53	0.56	0.46	0.44	0.43
4	LPPE 1F-II, 120°C.	2.21	2.06_2	2.19_1	2.33	0.67	0.73	0.61
5	LPPE 1F-III, 120°C.	0.44	0.46_3	0.43_7	0.34	0.44	0.45	0.46
6	EBC 1-I, 120°C.	1.31	1.30_7	1.32_2	1.40	0.44	0.45	0.45
7	HPPE 1-II, 120°C.	1.23	1.20_0	1.22_4	1.29	0.50	0.51	0.49
8	HPPE 2-II, 120°C.	0.92	0.94_0	0.94_8	0.91	0.30	0.30	0.29
9	HPPE 3-II, 120°C.	1.09	1.11_3	1.09_3	—	0.41	0.40	0.43
10	EBC 2-II, 120°C.	1.04	1.01_9	1.06_2	—	0.39	0.41	0.41
11	LPPE 1F-III, 140°C.	2.86	—	2.82_7	—	0.95	—	0.99
12	PP 1-II, 120°C.	2.22	—	2.24_0	—	0.37	—	0.35
13	PP 2-IV, 135°C.	3.02	—	3.06_3	—	0.45	—	0.42

[a] Solvents Code: I, α-chloronaphthalene; II, tetralin; III, α-methyl naphthalene; IV, decalin. Solute Code: LPPE, low pressure polyethylene (F denotes fraction); HPPE, high pressure polyethylene; EBC, ethylene-butene copolymer; PP, polypropylene.

TABLE II
Comparison of Two-Point Viscosity Values with Single-Point Evaluation Showing Per Cent Deviation
from Graphical Value of $[\eta]$

System	$[\eta]$, dl./g.				
				Single-point evaluation[a]	
	Graph	2 point form	Computer	Exponential	$k = 0.5$
1	1.38	1.39$_7$	1.35$_6$	1.47	1.47
% deviation	—	1.2	−1.7	6.5	6.5
3	0.53	0.53$_1$	0.52$_7$	0.53$_6$	0.50$_9$
% deviation	—	0.2	−0.6	1.1	−4.0
4	2.21	2.19$_1$	2.06$_2$	2.21$_0$	2.25
% deviation	—	−0.8	−6.7	0	1.8
6	1.31	1.32$_2$	1.30$_7$	1.28$_6$	1.30$_5$
% deviation	—	0.9	−0.2	−1.8	−0.4
7	1.23	1.22$_4$	1.20$_0$	1.21$_0$	1.22$_6$
% deviation	—	−0.5	−2.4	−1.6	−0.3
8	0.92	0.94$_3$	0.94$_0$	0.98$_9$	1.00
% deviation	—	2.5	2.2	7.5	8.8
10	1.04	1.06$_2$	1.01$_9$	1.07$_7$	1.08$_2$
% deviation	—	2.1	−2.0	3.6	4.0
11	2.86	2.82$_7$	—	3.22$_0$	3.36
% deviation	—	−1.1	—	12.6	17.5
12	2.22	2.24$_0$	—	2.21$_4$	2.27$_4$
% deviation	—	0.9	—	−0.3	2.4
13	3.02	3.06$_3$	—	2.91$_3$	2.88
% deviation	—	1.4	—	−3.5	−4.6
Mean deviation (%)		1.1$_6$	2.2$_6$	3.8$_5$	5.0$_3$

[a] Using exponential form method and Huggins equation with $k = 0.5$, at solute concentrations less than 0.15 g./100 ml., as suggested in ref. 4.

tion limits having demonstrably satisfied the demands of eq. (2).

The feasibility of reliably calculating k values by the two-point method establishes its clear advantage over previously described single-point $[\eta]$ calculations. In the present systems it can also be demonstrated that $[\eta]$ itself is more accurately obtained by the two-point form than by some single-point methods. In Table II, intrinsic viscosities computed by the techniques of this work are compared with values calculated from two single-point methods, recently described by Thomas and Thomas.[4] In the first of these, it is assumed that the exponential form $\eta = \eta_0 e^{[\eta]c}$ is a good representation of the experimental data when solute concentrations are of the order of 0.13 g./dl. or less. In the second, a value of 0.5 is assigned to k. Both methods were reported to give $[\eta]$ values in excellent agreement with extrapolated intrinsic viscosities for a number of polymer-solvent systems.[4]

Table II represents results only for those systems in which data were available at solute concentrations less than 0.15 g./dl. The tabulation confirms the previous authors' conclusion[4] that the exponential fit provides a more accurate $[\eta]$ evaluation than the single-point method based on $k = 0.5$. Obviously, however, neither of the single-point methods is a serious rival, in these cases, to the reliability of the two-point form. This may be seen by inspection of the per cent deviation figures quoted in Table II. These figures are based on a comparison of the various computed $[\eta]$ values with the graphical evaluation. The procedure

seems justified since the systems were chosen originally because extrapolations of both η_{sp}/c vs. c and $\ln \eta_r/c$ vs. c plots resulted in virtually identical $[\eta]$ figures. The two-point form has, in fact, a clear superiority over all other methods of data processing, including in these cases the values derived from the simple computer program.

From the variety of systems investigated here, it is concluded that concentrations near the limits of the range $0.15 < c < 0.6$ g./dl. should result in accurate viscosity parameter evaluations in many polymer-solvent systems using the two-point method. It would seem possible that in systems having $[\eta]$ values much above the limits of the range investigated, a shift toward lower concentration values would be convenient. Such matters can be quickly resolved, of course, by a small number of suitable calibration experiments.

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H. P. SCHREIBER
S. H. STOREY
H. W. HOLDEN

Central Research Laboratory
Canadian Industries Limited,
McMasterville, Quebec, Canada

On the Crystal Transformation of Poly [3,3-(bis-chloromethyl) oxacyclobutane]

The crystalline structure of poly [3,3-(bis-chloromethyl)-oxacyclobutane] was investigated by Sandiford.[1] According to his study, two crystal forms, α and β, are found in the polymer: The α form results when the polymer is annealed through its molten state, whereas the quenched amorphous polymer crystallizes into the β-form when its temperature is raised above the glass transition temperature.

Sandiford gave the unit cell dimensions of the β form (monoclinic) as $a = 6.85$, $b = 11.42$, and $c = 4.75$ A., and $\beta = 109°48'$. However, he did not refer to the dimensions of the α form. Recently Hatano and Kambara[2] investigated the crystal forms of the polymer with x-ray diffractometry and found the crystallizing behavior to be the same as that reported by Sandiford. However, the phenomena of the transformations between the α and β forms have never been examined.

In the present work, the crystallizing behavior and the transformation of crystal forms of this polymer were studied with x-ray diffractometry and infrared spectroscopy. X-ray diffraction curves of the α and β forms are shown in Figure 1 as A and B respectively. Film sample A was prepared by annealing at 160°C. for 3 hr. through its molten state, and then slow cooling to 120°C. during a period of 4 hr. Sample B was heat-treated at 113°C. during a period of 6$\frac{1}{2}$ hr., having first been quenched through its molten state in ice water. The patterns of x-ray diffraction of sample A and sample B agree with those of the α and β forms examined by Hatano and Kambara.[2] The original film samples were obtained from a cyclohexanone solution of the polymer which had been cast into film at 100°C. With respect to the x-ray diffraction curve of sample D, (hot-pressed, 200 kg./cm.² at 190°C.), Figure 1, its crystal is almost the same as the β form. The curve of sample E, which had been crystallized for several hours at room temperature after having first been quenched in ice water, is almost identical with that of sample B. This experimental result shows that (1) the quenched amorphous polymer is
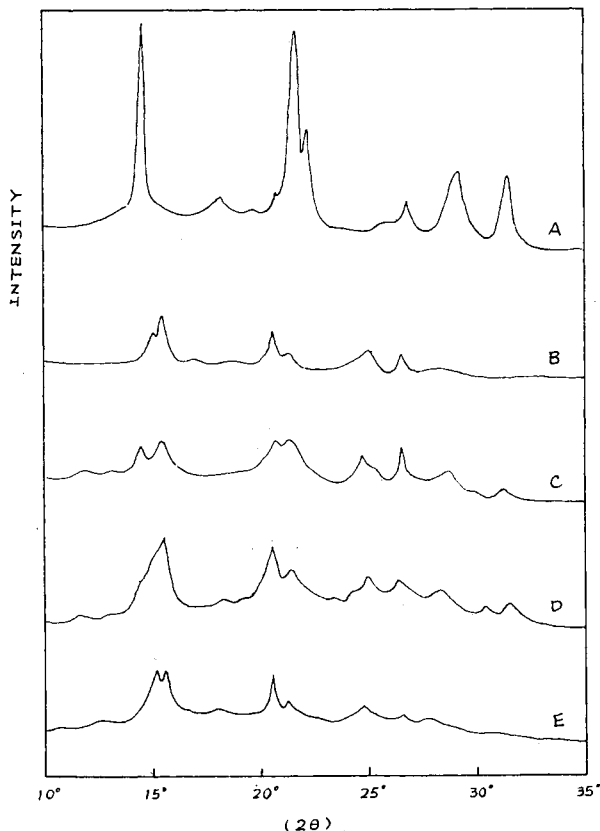
Fig. 1. X-ray diffraction curves under various crystallizing conditions: (A) annealed through molten state; (B) crystallized at 113°C. after quenching; (C) cast from cyclohexanone solution; (D) hot-pressed; (E) crystallized at room temperature after quenching.
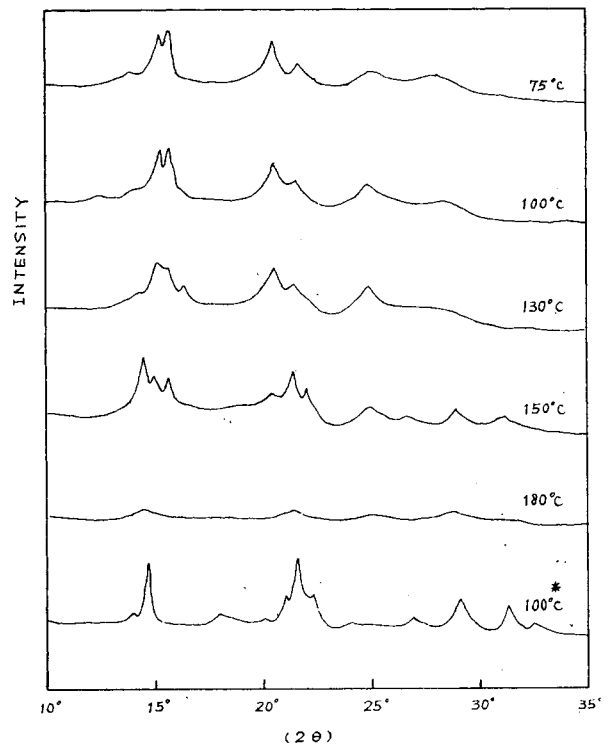
Fig. 2. Effect of temperature on x-ray diffraction curve of the sample E. Temperature of the sample was raised from room temperature up to 180°C.; (*) gradually cooled to 100°C. after having been kept at 180°C.