

# A New Analytical Method to Calculate Intrinsic Viscosity and Viscosity Constants of Polymer–Solvent Systems

UDAYA S. TOTI, KRISHNA S. AMUR, MAHADEVAPPA Y. KARIDURAGANAVAR, LATA S. MANJESHWAR, MRITYUNJAYA I. ARALAGUPPI, TEJRAJ M. AMINABHAVI

Department of Chemistry, Polymer Research Group, Karnatak University, Dharwad 580003, India

Received 2 January 2001; accepted 18 February 2001

**ABSTRACT:** Experimental viscosities were measured by Schott Gerate viscometer at 30 °C for polystyrene–chloroform and polycaprolactum–benzene systems. These data were analyzed by a newly developed analytical method to calculate intrinsic viscosity and viscosity constants. The analytical method was compared with the graphical as well as the least squares methods and the new analytical method is better than the graphical method because it avoids personal errors that might arise in reading the intercept and slope values from the reduced viscosity versus concentration plots. Furthermore, the analytical method is as effective as the least squares method, but provides better insights while choosing the experimental viscosity values. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 283–290, 2002

**Key words:** intrinsic viscosity; viscosity constants; polystyrene; polycaprolactum

## INTRODUCTION

In a previous study,<sup>1</sup> we developed the analytical method for the treatment of osmometric data on polymer–solvent systems. In continuation of this research, we now present a similar, but slightly different theory that can be used for the analysis of viscosity data of polymer–systems. In the viscometric method, viscosity,  $\eta$ , of a polymer solution of different concentrations is measured, and the intrinsic viscosity,  $[\eta]$ , as well as viscosity average molecular mass,  $\overline{M}_\eta$  can be calculated by the graphical method. Several empirical methods have been used<sup>2–6</sup> to estimate the molar mass of polymers in solution. The most commonly used approach is that of Huggin, which is given as:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2c \quad (1)$$

Another approach follows from Kraemer's equation, given in the form:

$$\ln\left(\frac{\eta_{sp}}{c}\right) = [\eta] - k_1[\eta]^2c \quad (2)$$

Thus, the graphs of  $\eta_{sp}/c$  versus  $c$  or  $\ln \eta_{sp}/c$  versus  $c$  using eqs. 1 and 2, respectively, yield the straight lines; by extrapolating the lines to a common intercept on the ordinate axis such that  $k_H + k_1 \cong 0.5$ , intrinsic viscosity,  $[\eta]$  can be calculated. On the contrary, the experimental results do not quite follow eqs. 1 and 2 and, therefore, it becomes necessary to use the equations that contain higher order virial coefficients given by the following relations:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2c + k'_H[\eta]^3c^2 \quad (3)$$

$$\ln\left(\frac{\eta_{sp}}{c}\right) = [\eta] - k_1[\eta]^2c - k'_1[\eta]^3c^2 \quad (4)$$

Correspondence to: Tejraj M. Aminabhavi (aminabhavi@yahoo.com; cc to rrist@sancharnet.in; rrist@bgl.vsnl.net.in).

*Journal of Applied Polymer Science*, Vol. 83, 283–290 (2002)  
© 2002 John Wiley & Sons, Inc.

Equations 1–4 have been routinely used in the polymer literature for the analysis of viscosity data. Alternatively, we now suggest the use of the newly developed analytical method (AM) to estimate the parameters of eqs. 3 and 4. It is realized that the analytical method proposed next is more satisfactory than the conventional graphical method (GM) as well as the least squares method (LSM).

## PROPOSED ANALYTICAL METHOD

Let us suppose that in a viscometric experiment, we have a pair of experimental points  $(c, \eta_r)$ , which form a mathematical set defined by:

$$S = \{(c_i, \eta_{r(i)}), \quad i = 1, 2, 3 \dots p\} \quad p \geq 2 \quad (5)$$

An expeditious method is to plot the graph of  $\eta_{sp}/c$  versus  $c$ , which gives a linear graph, the intercept on the ordinate axis gives  $[\eta]$ , whereas the slope gives  $k_H[\eta]^2$ . Such graphical procedures are subjected to approximations and may lead to manual errors. However, the least squares methods generally take care of such small errors. The analytical approach suggested here will replace the graphical evaluation of the parameters of eqs. 1–4. Even though the use of eqs. 3 and 4 gives values of  $[\eta]$  and the virial expressions that are more accurate than those obtained by the graphical method (eqs. 1 and 2), yet some discrepancies may exit in the final values probably due to the nonideality of the polymer solutions.

To develop the new equation, let  $(c_i, \eta_{r(i)})$  and  $(c_j, \eta_{r(j)})$  be any two points in  $S$ , with  $1 \leq i \leq j \leq p$ . Then, from eq. 1 we can obtain two simultaneous equations in  $[\eta]$  and  $[\eta]^2 k_H$ . Solving them and setting  $(\eta_{sp(i)}/c_i) = N_i$ , we get,

$$\begin{aligned} [\eta]_{H(i,j)} &= (N_j c_i - N_i c_j)/(c_i - c_j) \\ [\eta]_{H(i,j)}^2 k_{H(i,j)} &= (N_i - N_j)/(c_i - c_j) \end{aligned} \quad (6)$$

Here, we have denoted  $[\eta]$  obtained by Huggins formula (eq. 1), using the observation points  $(c_i, \eta_{r(i)})$  and  $(c_j, \eta_{r(j)})$  by  $[\eta]_{H(i,j)}$ . Following the same procedure for eq. 2 and setting  $\ln \eta_{r(i)} = L_i$  we get,

$$\begin{aligned} [\eta]_{k(i,j)} &= (L_j c_i - L_i c_j)/(c_i - c_j) \\ [\eta]_{k(i,j)}^2 k_{1(i,j)} &= (L_j - L_i)/(c_i - c_j) \end{aligned} \quad (7)$$

Because the indices  $i, j$  take the values from 1 to  $p$ , and  $i < j$ , the number of each of the aforementioned parameters is  $p!/(p-2)!$  so that  $(p-2)!/p! = A$ , and by taking the average values, we get

$$[\eta]_H = A \sum_{i < j} [\eta]_{H(i,j)} \quad k_H = A \sum_{i < j} k_{H(i,j)} \quad (8)$$

and

$$[\eta]_k = A \sum_{i < j} [\eta]_{k(i,j)} \quad k_1 = A \sum_{i < j} k_{1(i,j)} \quad (9)$$

Thus, the extrapolation of straight lines using eqs. 1 and 2 should meet at a point on the ordinate axis, such that  $[\eta]_H = [\eta]_k$ , but the common value at the intersection is the intrinsic viscosity.

Generally, there is a good agreement between the values of the parameters obtained by the graphical method and those obtained by calculations using the formulae just given. However, noticeable deviations may occur in first and second virial coefficients, but not so with the intrinsic viscosity values, probably because of the inaccuracies in the graphical approach while reading the intercept and determining the slope. Sometimes<sup>7</sup> experimental results do not conform to the aforementioned expectations, because the real relationships are actually of the form shown in eqs. 3 and 4, of which eqs. 1 and 2 are the truncated versions. No two-parameter solution, such as given in eqs. 8 and 9, is universally valid because it forces a real curvilinear relation into a rectilinear form. In view of this, here we solve eqs. 3 and 4 using the simple analytical method presented below:

Let  $(c_1, \eta_{r(1)})$ ,  $(c_2, \eta_{r(2)})$ , and  $(c_3, \eta_{r(3)})$  be three observation points. We solve for  $[\eta]_H^2 k_H$  and  $[\eta]_H^2 k'_H$  in the first instance, from the following equations obtained from eq. 3,

$$N_i = [\eta]_H + k_H [\eta]_H^2 c_i + k'_H [\eta]_H^3 c_i^2 \quad i = 1, 2, 3 \quad (10)$$

where  $N_i$  has the same meaning as before. From the first two terms in eq. 10 corresponding to  $i = 1, 2$ , we have

$$k_H [\eta]_H^2 = \{N_2 c_1^2 - N_1 c_2^2 - (c_1^2 - c_2^2)[\eta]_H\}/c_1 c_2 (c_1 - c_2) \quad (11)$$

and

**Table I Viscosity Data of Polymer-Solvent Systems**

Data Points	Concentration, $C$ (g/dL)	Flow Time, $t$ (s)	$t/t_0 = \eta_r$	$N = \eta_{sp}/C$	$L = \ln \eta_r/C$
I Polymethylmethacrylate in benzene at 30°C (flow time for solvent, $t_0 = 216.0$ s)					
1	0.2716	459.8	2.1287	4.156	2.782
2	0.1940	378.2	1.7509	3.870	2.887
3	0.1509	337.9	1.5644	3.740	2.966
4	0.1235	312.8	1.4481	3.629	2.998
5	0.1045	296.4	1.3722	3.562	3.028
II Polycaprolactum in benzene at 30°C (flow time for solvent, $t_0 = 18.66$ s)					
1	0.0702	51.74	2.773	25.25	14.52
2	0.0503	39.98	2.143	22.27	15.15
3	0.0250	27.78	1.489	19.54	15.91
4	0.0201	25.70	1.377	18.78	15.94
5	0.0151	23.84	1.278	18.31	16.27
III Polystyrene in chloroform at 30°C (flow time for solvent, $t_0 = 10.60$ s)					
1	0.020	14.98	1.4132	82.64	69.17
2	0.015	20.43	1.9274	92.74	65.62
3	0.010	27.23	2.5689	104.6	62.90
4	0.005	34.98	3.300	115.0	59.70

$$k'_H[\eta]_H^3 = -\{N_2c_1 - N_1c_2 - (c_1 - c_2)[\eta]_H\} \\ \div c_1c_3(c_1 - c_2) \quad (12)$$

On the other hand, from the first and third terms in eq. 10, we get

$$k'_H[\eta]_H^3 = -\{N_3c_1 - N_1c_3 - (c_1 - c_3)[\eta]_H\} \\ \div c_1c_3(c_1 - c_3) \quad (13)$$

After routine calculations, using eqs. 12 and 13 we find that

$$[\eta]_H^3 = -\{N_1c_2c_3(c_2 - c_3) + N_2c_3c_1(c_3 - c_1) \\ + N_3c_1c_2(c_1 - c_2)\}/Z \quad (14)$$

where  $Z = (c_1 - c_2)(c_2 - c_3)(c_3 - c_1)$ .

Substituting the expression for  $[\eta]_H$  in eqs. 11 and 12, we get

$$[\eta]_H^2k_H = \{N_1(c_2^2 - c_3^2) + N_2(c_3^2 - c_1^2) + N_3(c_1^2 - c_2^2)\}/Z \quad (15)$$

$$[\eta]_H^3k'_H = -\{N_1(c_2 - c_3) + N_2(c_3 - c_1) \\ + N_3(c_1 - c_2)\}/Z \quad (16)$$

In a similar manner, we obtain the following set of relations from eq. 4:

$$[\eta]_k = -\{L_1c_2c_3(c_2 - c_3) + L_2c_3c_1(c_3 - c_1) \\ + L_3c_1c_2(c_1 - c_2)\}/Z \quad (17)$$

$$[\eta]_k^2k_1 = -\{L_1(c_2^2 - c_3^2) + L_2(c_3^2 - c_1^2) \\ + L_3(c_1^2 - c_2^2)\}/Z \quad (18)$$

$$[\eta]_k^3k'_1 = -\{L_1(c_2 - c_3) + L_2(c_3 - c_1) \\ + L_3(c_1 - c_2)\}/Z \quad (19)$$

If the set  $S$  given in eq. 5 consists of more than three points, then it is denoted by  $[\eta]_{H(i,j,k)}$ ,  $k_{H(i,j,k)}$ , etc., and the corresponding parameter value is determined by the points  $(c_i, \eta_{r(i)})$ ,  $(c_j, \eta_{r(j)})$ , and  $(c_k, \eta_{r(k)})$  in  $S$ , where  $1 \leq i \leq j \leq k \leq p$  and  $p \leq 3$ . However, in this case, there are  $p!/(p-3)!$  values of these parameters and thus, taking the average over these values, we get

$$[\eta]_H = B \sum_{i < j < k} [\eta]_{H(i,j,k)} \quad k_H = B \sum_{i < j < k} k_{H(i,j,k)} \\ k'_H = B \sum_{i < j < k} k'_{H(i,j,k)} \quad (20)$$

where we have set  $(p - 3)!3!/p! = B$ .

A similar set of relations can be derived for  $[\eta]_k$ ,  $k_1$ , and  $k'_1$ . Thus, we have

$$\begin{aligned} [\eta]_k &= B \sum [\eta]_{k(i,j,k)} & k_1 &= B \sum k_{1(i,j,k)} \\ k'_1 &= B \sum k'_{1(i,j,k)} \end{aligned} \quad (21)$$

Here, the summation is taken over the range as indicated in eq. 21. While taking the averages, one should carefully examine different values of each of the parameters and look for those values, which deviate significantly from the majority of other values, and then try to identify those observation points that introduce such deviations. Such points correspond to the faulty data and should be ignored. The average may then be taken over the number of values determined by the remaining points.

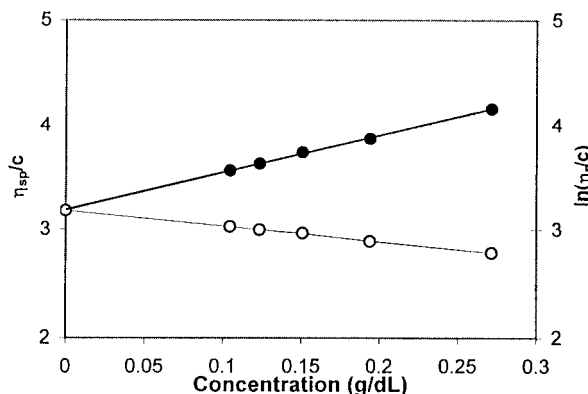
## EXPERIMENTAL

### Materials

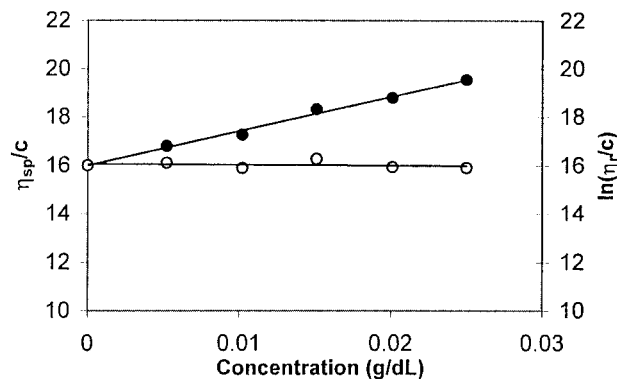
Polystyrene was obtained from General Electric Company. Polycaprolactum, chloroform, and benzene were of AR grade samples, purchased from s.d. fine Chemicals Ltd., Mumbai, India.

### Viscosity Measurement

Solutions of known concentration of polystyrene in chloroform and polycaprolactum in benzene were prepared at different concentrations. The solvent flow time,  $t_o$  and the solution flow time,  $t$ , for different concentrations,  $c_i$ ,  $c_j$ ,  $c_k$ ...etc., were



**Figure 1** Plots of  $\eta_{sp}/c$  (●) and  $\ln \eta_{sp}/c$  (○) versus concentration of polymethylmethacrylate in benzene at 30°C.

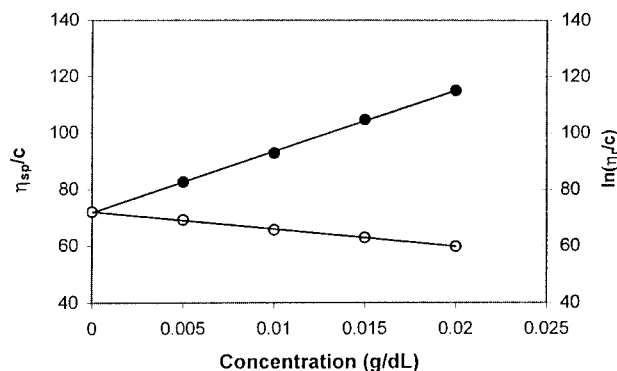


**Figure 2** Plots of  $\eta_{sp}/c$  (●) and  $\ln \eta_{sp}/c$  (○) versus concentration of polycaprolactum in benzene at 30°C.

measured at 30°C with a Schott-Gerate viscometer (Model AVS 350, Germany).<sup>8</sup> The viscometry constant used was  $0.03174 \text{ mm}^2/\text{s}^2$ . The measured viscosity values are presented in Table I. In case of polymethylmethacrylate in benzene, viscosity data were taken from the literature.<sup>9</sup> The graphical method is applicable to eqs. 1 and 2 only. The graphs corresponding to these for all the systems are given in Figures 1–3. The values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  were obtained from the intersections on the ordinate axis and slopes of the linear graphs. Calculated values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  are compared with the analytical method in Table II. We have also computed the values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  by the least squares method (LSM) and compared the results with those of the analytical method (AM).

## RESULTS AND DISCUSSION

In the proposed AM, the following steps led us to the required results:



**Figure 3** Plots of  $\eta_{sp}/c$  (●) and  $\ln \eta_{sp}/c$  (○) versus concentration of polystyrene in benzene at 30°C.

**Table II** Calculated Values of Equations 6 and 7 from Experimental Data

$(i, j)$	Equation 6		Equation 7		$k_{H(i,j)} + k_{1(i,j)}$
	$[\eta]_{H(i,j)}$	$k_{H(i,j)}$	$[\eta]_{k(i,j)}$	$k_{1(i,j)}$	
I Polymethylmethacrylate in benzene at 30°C					
(1, 2)	3.1550	0.3703	3.1495	0.1364	0.5067
(1, 3)	3.2199	0.3324	3.1960	0.1492	0.4817
(1, 4)	3.1895	0.3498	3.1781	0.1444	0.4942
(1, 5)	3.1905	0.3492	3.1818	0.1454	0.4946
(2, 3)	3.2848	0.2795	3.2426	0.1743	0.4539
(2, 4)	3.2068	0.3324	3.1924	0.1545	0.4869
(2, 5)	3.2023	0.3356	3.1926	0.1546	0.4901
(3, 4)	3.1286	0.4138	3.1422	0.1183	0.5321
(3, 5)	3.1611	0.3839	3.1676	0.1332	0.5171
(4, 5)	3.1935	0.3458	3.1930	0.1549	0.5006
II Polycaprolactum in benzene at 30°C					
(1, 2)	16.33	0.4770	16.74	0.1129	0.5900
(1, 3)	16.56	0.4519	16.84	0.1165	0.5684
(1, 4)	15.38	0.4707	16.68	0.1105	0.5813
(1, 5)	16.18	0.4930	16.51	0.1040	0.5970
(2, 3)	16.71	0.4278	16.91	0.1221	0.5499
(2, 4)	16.40	0.4675	16.66	0.1081	0.5757
(2, 5)	16.16	0.4997	16.47	0.0965	0.5962
(3, 4)	16.17	0.5145	16.49	0.0849	0.5994
(3, 5)	15.94	0.5555	16.30	0.0665	0.6219
(4, 5)	15.66	0.6323	16.06	0.0237	0.6560
III Polystyrene in chloroform at 30°C					
(1, 2)	73.36	0.3867	72.50	0.1218	0.5085
(1, 3)	70.48	0.4481	71.54	0.1156	0.5637
(1, 4)	71.85	0.4179	72.32	0.1207	0.5386
(2, 3)	69.04	0.4972	71.06	0.1077	0.6049
(2, 4)	71.67	0.4273	72.31	0.1199	0.5472
(3, 4)	72.54	0.3839	72.72	0.1343	0.5182

(i) Using eqs. 6 and 7, we obtain the values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  with different combination of  $i$  or  $j$ , and these are listed in Table II.

(ii) Using eqs. 14–16 and eqs. 17–19, the values of  $[\eta]_{H(i,j,k)}$ ,  $k_{H(i,j,k)}$ ,  $k'_{H(i,j,k)}$ , and  $[\eta]_{k(i,j,k)}$ ,  $k_{1(i,j,k)}$ ,  $k'_{1(i,j,k)}$  were obtained, and these are listed in Table III.

In case of polymethylmethacrylate in benzene system, the values of  $[\eta]_{H(i,j)}$  and  $k_{H(i,j)}$  with different combination of  $i$  or  $j$ , vary from 3.1287 to 3.2848 and from 0.2795 to 0.4138, respectively. So also the values of  $[\eta]_{k(i,j)}$  and  $k_{1(i,j)}$  vary from 3.1432 to 3.2426 and from 0.1183 to 0.1783, respectively. These variations are certainly too wide and reveal the erratic behavior of  $(c_3, \eta_{R(3)})$  that force us to ignore  $(c_3, \eta_{R(3)})$  while computing the

values of the required parameters (see Table II). The data obtained from eqs. 14–16 and eqs. 17–19 display again an erratic behavior of  $(c_3, \eta_{R(3)})$  and indicate that observation point 2 is another such a candidate (see Table III). This behavior can also be seen in Table II where  $[\eta]_{H(1,2)} = 3.1550$  and  $[\eta]_{H(2,4)} = 3.2068$ .

Different methods using eqs. 6 and 7 are compared in Table IV. Data in Table I are chosen in the sequences of 1,4,5; 1,2,4,5 and all the five points. As is required with the AM, the average is taken over the range of corresponding sequences to determine the values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$ . The choice of sequences provides a comparison of the results obtained from the well-behaved points with those obtained from all the points. We have also computed the values of  $[\eta]_H$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  for the sequences specified above by the LSM. The

**Table III** Calculated Values of Equations 14–19

$(i, j, k)$	Eq. 14 $[\eta]_{H(i,j,k)}$	Eq. 15 $k_{H(i,j,k)}$	Eq. 16 $k'_{H(i,j,k)}$	Eq. 17 $[\eta]_{H(i,j,k)}$	Eq. 18 $k_{1(i,j,k)}$	Eq. 19 $k'_{1(i,j,k)}$	$k_{H(i,j,k)} + k_{1(i,j,k)}$	$k'_{H(i,j,k)} + k'_{1(i,j,k)}$
I Polymethylmethacrylate in benzene at 30°C								
(1, 2, 3)	3.4472	0.0929	0.1354	3.3590	0.2840	-0.1049	0.3769	0.0305
(1, 2, 4)	3.2500	0.2694	0.0525	3.2283	0.1966	-0.0444	0.4660	0.0081
(1, 2, 5)	3.2320	0.2877	0.0433	3.2196	0.1903	-0.0399	0.4780	0.0034
(1, 3, 4)	3.0526	0.5549	-0.1435	3.0974	0.0529	0.0810	0.6078	-0.0625
(1, 3, 5)	3.1242	0.4540	-0.0765	3.1499	0.1057	0.0360	0.5597	-0.0404
(1, 4, 5)	3.1960	0.3410	0.0059	3.2023	0.1700	-0.0220	0.5110	-0.0161
(2, 3, 4)	2.8551	0.9910	-0.6307	3.9664	-0.1614	0.3614	0.8296	-0.2693
(2, 3, 5)	3.0166	0.6787	-0.3337	3.0800	-0.0086	0.1899	0.6701	-0.1438
(2, 4, 5)	3.1780	0.3764	-0.0376	3.1936	0.1559	-0.0015	0.5323	-0.0391
(3, 4, 5)	3.3395	0.0850	0.3037	3.3000	0.3290	-0.2449	0.4140	0.0588
II Polycaprolactum in benzene at 30°C								
(1, 2, 3)	17.10	0.3438	0.0441	17.07	0.1471	-0.0187	0.4909	0.0253
(1, 2, 4)	16.44	0.4562	0.0072	16.62	0.0990	0.0078	0.5553	0.1500
(1, 2, 5)	16.09	0.5210	-0.0159	16.36	0.6890	0.0251	0.5909	0.0091
(1, 3, 4)	15.96	0.5847	-0.0585	16.29	0.0368	0.0510	0.6214	-0.0075
(1, 3, 5)	15.69	0.6509	-0.0894	16.08	0.0023	0.0740	0.6532	-0.0154
(1, 4, 5)	15.37	0.7658	-0.1581	15.82	-0.0642	0.1243	0.7017	-0.3380
(2, 3, 4)	15.65	0.6978	-0.1564	16.07	-0.0199	0.1125	0.6779	-0.0390
(2, 3, 5)	15.43	0.7605	-0.1957	15.89	-0.0557	0.1424	0.7048	-0.0533
(2, 4, 5)	15.17	0.8645	-0.2788	15.67	-0.1206	0.2060	0.7439	-0.0728
(3, 4, 5)	15.07	0.9591	-0.3976	15.51	-0.1824	0.0297	0.7767	-0.1004
III Polystyrene in chloroform at 30°C								
(1, 2, 3)	64.72	0.7377	-0.1062	69.62	0.0627	0.0285	0.8004	-0.0778
(1, 2, 4)	71.11	0.4637	-0.0721	72.24	0.1168	0.0023	0.5805	-0.0187
(1, 3, 4)	73.23	0.3364	0.0350	73.11	0.1543	-0.0201	0.4907	0.0148
(2, 3, 4)	74.29	0.2709	0.8536	73.55	0.1773	-0.0417	0.4482	0.0436

corresponding results are compared in Tables IV with LSM. A close agreement is found between the AM and LSM, but the results of GM differ slightly from those of AM and LSM.

The results obtained from AM (from eqs. 14–19) and results obtained from LSM by fitting the data to parabolic curves are compared in Table V. Here, we find divergent results for different sequences. Thus, dropping out the observation points that behave erratically in combination with other points becomes significant. The values for the sequence 1,4,5 listed for the AM and the LSM in Table V show a close agreement, whereas for the sequence 1,2,4,5, which contains the ill-behaved point (i.e., 2), the results are not consistent both for the AM and LSM. Considering the sequence of all five points, the LSM gives better results than the AM. In fact, the AM is sensitive to the ill-behaved points.

In the case of polycaprolactum in benzene,  $[\eta]_{H(i,j)}$  and  $[\eta]_{k(i,j)}$  values vary from 15.38 to 16.71

and 16.06 to 16.91, respectively. The  $k_{H(i,j)}$  and  $k_{1(i,j)}$  values vary from 0.4278 to 0.6323 and 0.0237 to 0.1221, respectively (see Table II). In this case, it is quite difficult to trace the ill-behaved points. However, the average of these values are close to both GM and LSM, except in case of  $k_1$  (see Table IV). The values of  $[\eta]_{H(i,j,k)}$ ,  $k_{H(i,j,k)}$ ,  $k'_{H(i,j,k)}$ , and  $[\eta]_{k(i,j,k)}$ ,  $k_{1(i,j,k)}$ ,  $k'_{1(i,j,k)}$ , and  $[\eta]_{H(i,j,k)}$  obtained with eqs. 14–16 and eqs. 17–19 are presented in Table III and are compared with the values obtained from LSM in Table V. A close observation of these points reveals the erratic behavior of the points 2 and 5. Observing the corresponding values of the sequence (1,2,3) in Table II supports the good behavior of these points except the (1,3) combination.

In the case of polystyrene in chloroform,  $[\eta]_{H(i,j)}$  and  $[\eta]_{k(i,j)}$  values vary from 69.04 to 73.36 and 0.3839 to 0.4481, respectively. Here, the  $k_{H(i,j)}$  and  $k_{1(i,j)}$  values vary from 71.06 to 72.72 and 0.1077 to 0.1343, respectively. The  $[\eta]_{H}$ ,  $k_H$ ,  $[\eta]_k$ , and  $k_1$  val-

**Table IV Comparison of Different Methods**

Method	$[\eta]_H$	$k_H$	$[\eta]_k$	$k_1$	$k_H + k_H$	Points Used
I Polymethylmethacrylate in benzene at 30°C						
A.M.	3.1912	0.3482	3.1843	0.1482	0.4965	1, 4, 5
L.S.M.	3.1901	0.3494	3.1803	0.1430	0.4924	1, 4, 5
A.M.	3.1896	0.3471	3.1812	0.1483	0.4954	1, 2, 4, 5
L.S.M.	3.1897	0.3484	3.1799	0.1461	0.4945	1, 2, 4, 5
A.M.	3.1932	0.3493	3.1836	0.1465	0.4958	All five
L.S.M.	3.1954	0.3456	3.1833	0.1467	0.4923	All five
G.M.	3.1800	0.3636	3.1800	0.1428	0.5064	All five
II Polycaprolactum in benzene at 30°C						
A.M.	16.15	0.4990	16.57	0.0946	0.5936	All five (Average)
A.M.	16.04	0.4790	16.67	0.1040	0.5830	(1, 3, 4) (Average)
L.S.M.	15.99	0.4908	16.13	-0.0271	0.5287	All five
G.M.	16.00	0.4692	16.00	-0.0313	0.5323	All five
III Polystyrene in chloroform at 30°C						
A.M.	71.49	0.4269	72.08	0.1200	0.5469	All four (Average)
A.M.	72.29	0.4106	72.38	0.1208	0.5314	(1, 2, 4) (Average)
L.S.M.	71.51	0.4260	72.13	-0.1197	0.3063	All four
G.M.	72.00	0.4409	72.00	-0.1070	0.3339	All four

ues corresponding to the points (1,4) and (2,4) are closer to the values obtained from the LSM and GM (see Table IV). The value corresponding to the points (1,2,4) is nearer to the LSM values (See Table V).

We have also performed some experiments at higher concentration of polycaprolactum and polystyrene, but these data are not presented in

view of the wide variations signifying the failure of the analytical method in a highly viscous solution. Nevertheless, the analytical approach proposed here is better than the conventionally used graphical method.

We thank the Department of Science and Technology [SP/S1/H-26/96(PRU)], New Delhi and All India Coun-

**Table V Comparison of Different Methods**

Method	$[\eta]_H$	$k_H$	$k'_H$	$[\eta]_k$	$k_1$	$k'_1$	$k_H + k_1$	Points Used
I Polymethylmethacrylate in benzene at 30°C								
A.M.	3.1960	0.3409	0.0059	3.2023	0.1700	-0.0221	0.5109	1, 4, 5
L.S.M.	3.1897	0.3497	0.0000	3.1800	0.1449	0.0000	0.4946	1, 4, 5
A.M.	3.2140	0.3186	0.0160	3.2140	0.1782	-0.0269	0.4968	1, 2, 4, 5
L.S.M.	3.2335	0.2878	0.0421	3.2203	0.1900	-0.0393	0.4778	1, 2, 4, 5
A.M.	3.1692	0.4131	-0.0687	3.1804	0.1002	-0.0211	0.5133	All five
L.S.M.	3.2011	0.3377	0.0054	3.1993	0.1640	-0.0155	0.5017	All five
II Polycaprolactum in benzene at 30°C								
A.M.	15.96	0.5847	-0.0585	16.29	0.0368	0.0510	0.6214	1, 3, 4
A.M.	15.78	0.6043	-0.1300	16.14	0.0531	0.0754	0.6517	All five (Average)
L.S.M.	16.02	0.5383	0.0259	15.96	0.0856	0.2354	0.6239	All five
III Polystyrene in chloroform at 30°C								
A.M.	71.11	0.4637	-0.0721	72.24	0.1168	0.0023	0.5805	1, 2, 4
A.M.	70.84	0.4522	0.1776	72.13	0.1278	-0.0078	0.5800	All four (Average)
L.S.M.	71.89	0.4071	0.0081	72.57	-0.1348	0.0092	0.2723	All four

cil for Technical Education New Delhi [8017/RDII/R&D/TAP/(832)98-99] for the financial support.

## REFERENCES

1. Amur, K. S.; Harlapur, S. F.; Aminabhavi, T.M. *Polymer* 1997, 38, 6417.
2. Flory, P.J.; Fox, T.G. Jr. *J Amer Chem Soc* 1951, 73, 1904.
3. Munk, P.; Halbrook, M.E. *Macromolecules* 1976, 9, 441.
4. McCarthy, K.J.; Buckhardt, C.W.; Parazak, D. P. *J Appl Polym Sci* 1987, 33, 1699.
5. Lutringer, G.; Weill, G. *Polymer* 1991, 32, 877.
6. Flory, P.J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, New York, 1953.
7. Rudin, A. *The Elements of Polymer Science and Engineering*; Academic Press: New York, 1982.
8. Aminabhavi, T.M.; Banerjee, K. *J Chem Eng Data* 1998, 43, 852.
9. Gowarikar, V.R.; Vishwanathan, N.V.; Sreedhar, J. *Polymer Science*; Wiley Eastern Ltd.: New Delhi, 1988.