Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Intrinsic Viscosity Studies on Dilute Solution of Some New Aromatic Polyamides in Sulfuric Acid at 30°C

Mohamed M. El-Banna[a]
[a] Chemistry Department, Faculty of Education, Alexandria University, Egypt

To cite this Article El-Banna, Mohamed M.(1995) 'Intrinsic Viscosity Studies on Dilute Solution of Some New Aromatic Polyamides in Sulfuric Acid at 30°C', Journal of Macromolecular Science, Part A, 32: 1, 357 — 368
To link to this Article: DOI: 10.1080/10601329508019181
URL: http://dx.doi.org/10.1080/10601329508019181

MACROMOLECULAR REPORTS, A32(SUPPL. 3), 357-368 (1995)

INTRINSIC VISCOSITY STUDIES ON DILUTE SOLUTION OF SOME NEW AROMATIC POLYAMIDES IN SULFURIC ACID AT 30°C

Mohamed M. El-Banna

Chemistry Department, Faculty of Education, Alexandria University,

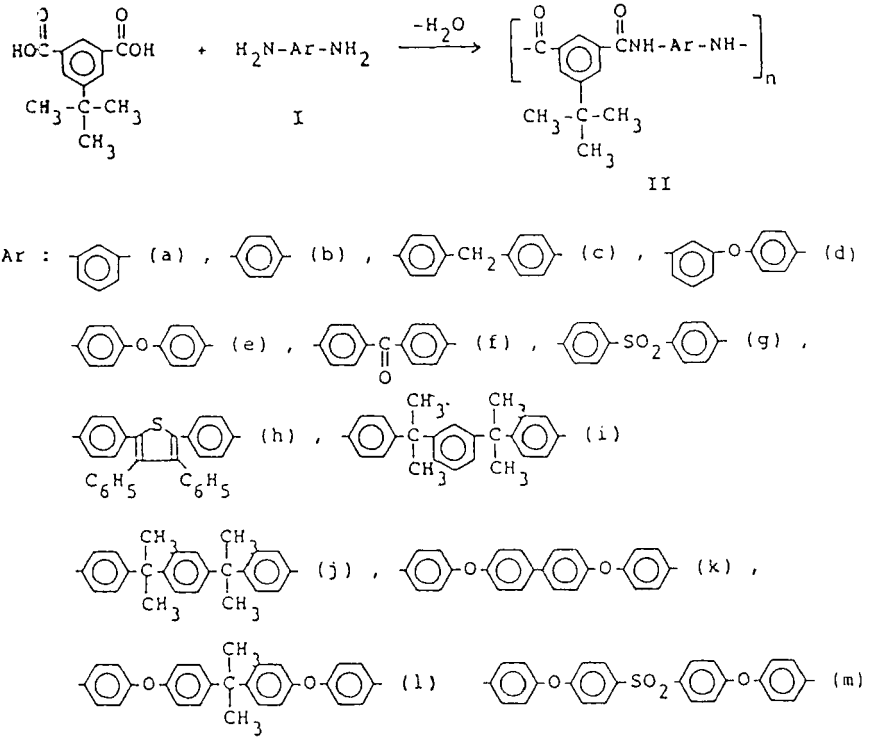
Egypt.

ABSTRACT

The intrinsic viscosity of some new polyamides (aramids)(1-4) are calculated by using single specific viscosity measurement at a concentration of 0.5 g/dl in concentrated sulfuric acid at 30°C. The connection between intrinsic viscosity and molecular weight is discussed in the light of the Flory and Fox theories. General procedures for treating intrinsic viscosity data are given. The root-mean square end-to-end distance of the chains as well as the radius of gyration are determined. In addition the relationship between the diffusion coefficient and the viscosity is obtained by Einstein method and the results are in agreement with Zhang and Murray. The mutual excluded volume is found to be smaller than the volume occupied by a polymeric coil and the polyamides included the Gaussian distribution characterizing the polymer in solution. The results provide a rigorous test of the recent theory relating the intrinsic viscosity to polymer chain structure and to the interaction between polymer and the solvent.

INTRODUCTION

In the treatment of the properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of chain elements, or segments, about the center of gravity. The average distribution of segments for a chain polymer molecule is approximately Gaussian; its breadth depends on the molecular chain length and on the thermodynamic interaction between polymer segments and solvent. The intrinsic viscosity may be regarded as a measure of the ratio of the effective hydrodynamic volume of the polymer in a given solvent to its number average molecular weight ($\bar{M}_n$). The recent theories [1-3] show that for sufficiently large chain lengths the effective hydrodynamic radius, r, must vary directly

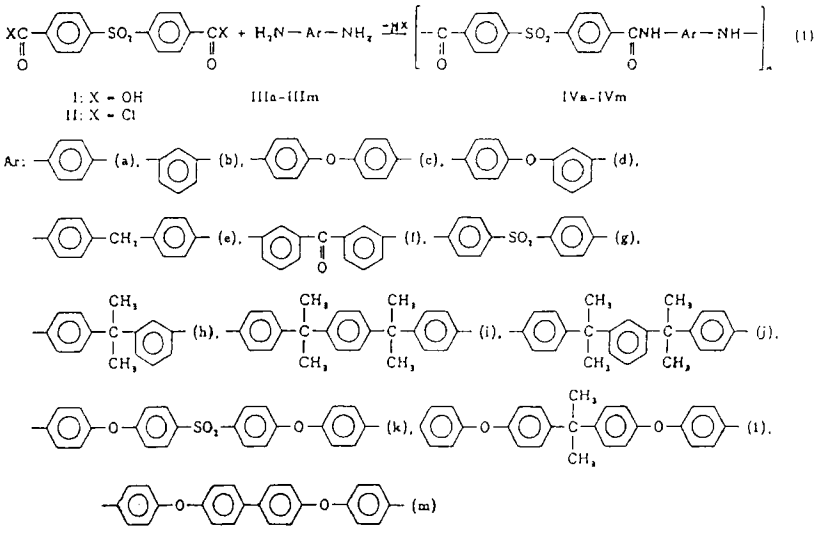


Scheme 1

with a linear parameter of the Gaussian distribution characterizing the polymer in solution. Convenient linear parameters for this purpose are the root-mean-square distance $\sqrt{h^2}$ between the ends of the polymer chain, or the root-mean-square distance $\sqrt{S^2}$ of the segments from the center of gravity (i.e., the radius of gyration of the dissolved molecule). The above conclusion had been anticipated previously by various authors [4].

Diffusion theories accounting for the free-volume diffusion models proposed by Vrentas et al [5,6] have been used previously to predict solvent self-diffusion and polymer-solvent binary mutual diffusion coefficients with the use of limited diffusion data [5,7] as well as with knowledge of solely pure polymer and solvent properties [8].

A series of some new aromatic polyamides(aramids) were previously prepared from :
1- 5-tButylisophthalic acid (BIPA) and various aromatic diamines [9]



Scheme 2

Aromatic polyamides were synthesized by the direct polycondensation of BIPA with various aromatic diamines in N-methyl-2-pyrrolidone (NMP) using triphenylphosphite (TPP) and pyridine (Py) as condensing agents (Scheme 1).

2- 4,4'-Sulfonyldibenzoic acid (SDBA) with various aromatic diamines [10]

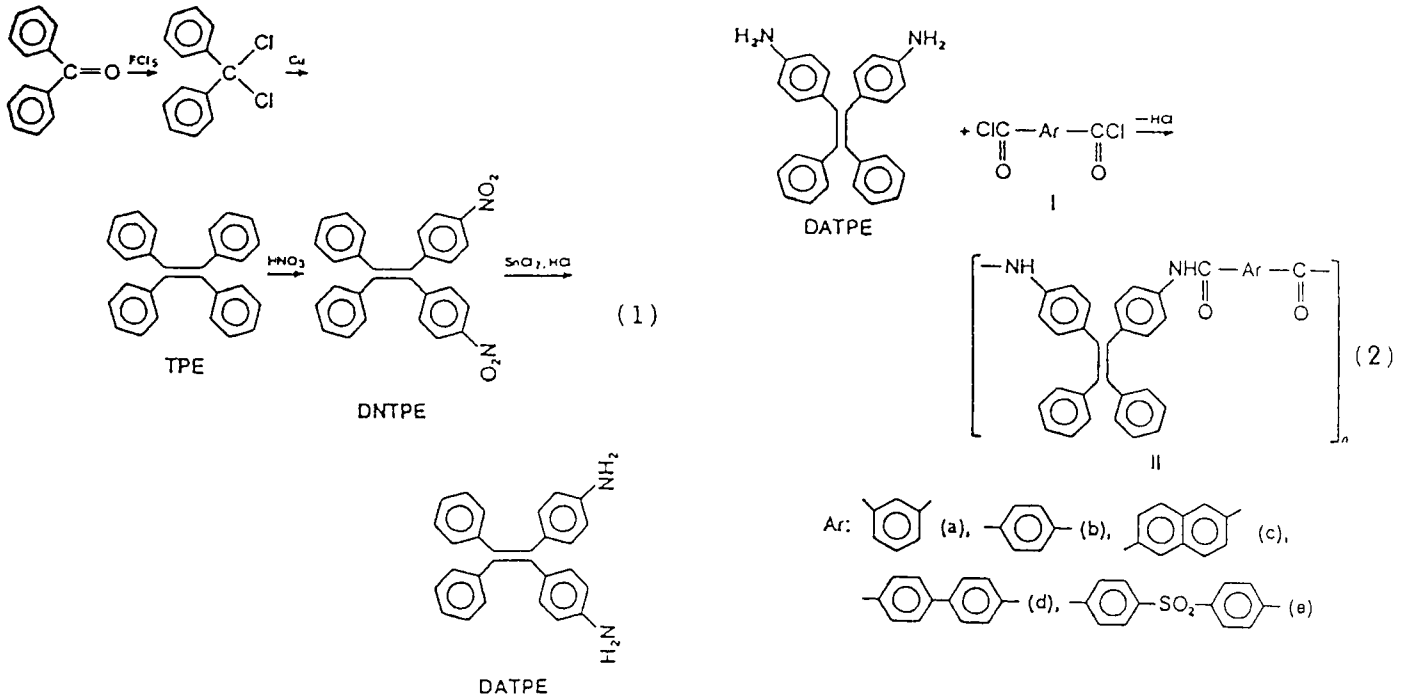
The aramids were prepared by the direct polycondensation of SDBA with various aromatic diamines using TPP and Py as condensing agents (Scheme 2).

3- 1,1-Bis(4-aminophenyl)-2,2-diphenylethylene (DATPE) and aromatic diacid chlorides [11].

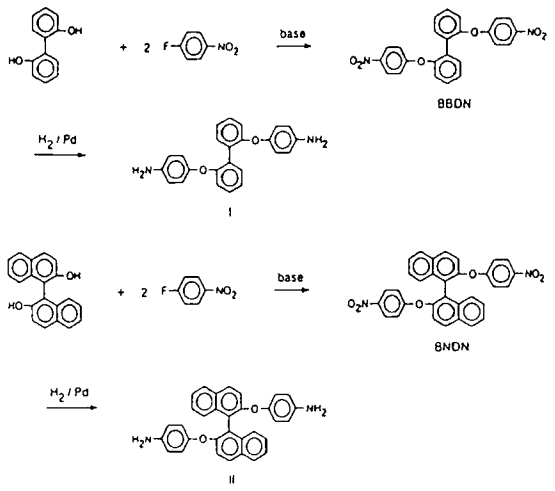
Novel aramids were prepared by the low temperature solution polycondensation of DATPE and aromatic diamines with various aromatic diacid chlorides (Scheme 3).

4- 2,2'-Bis(p-aminophenoxy) biphenyl (BBDA) I or 2,2'-bis(p-aminophenoxy)-1,1'-binaphthyl (BBDA) II and aromatic dicarboxylic acids[12]

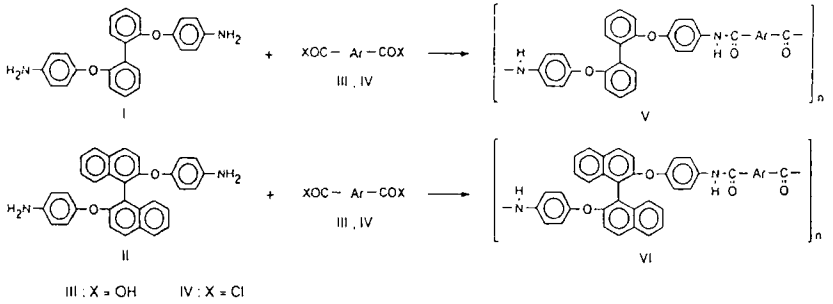
New aromatic diamines having kink and crank structures, (BBDA)I and (BBDA) II, were synthesized by the reaction of p-fluoronitrobenzene with biphenyl-2,2'-diol and 2,2'-dihydroxy-1,1'-binaphthyl,

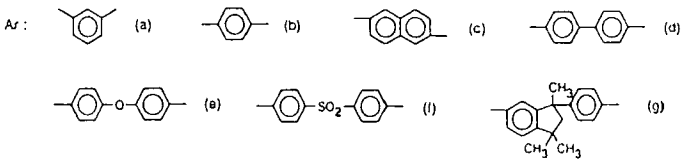


Scheme 3



"Method A"





"Method B"

Scheme 4

Table I : $[\eta]$, $\bar{M}_n$, r and $(h^2)^{\frac{1}{2}}$ values for the polyamides (1-4) in concentrated sulfuric acid.

Polymer code	$[\eta]$	$\bar{M}_n.10^{-4}$	$r.10^7$	$(h^2)^{\frac{1}{2}}.10^7$
		Polyamides (1)		
IIa	0.77	3.4	1.61	4.71
IIb	1.37	5.6	2.30	7.22
IIc	1.45	6.5	2.46	5.79
IId	1.31	3.7	1.97	10.67
IIe	2.79	10.9	3.64	5.46
IIf	1.10	3.7	1.86	3.69
IIg	0.74	1.7	1.26	6.89
IIh	1.32	6.2	2.35	6.85
IIi	1.07	7.5	2.33	5.96
IIj	1.00	5.3	2.03	13.34
IIk	3.49	17.0	4.55	10.38
III	2.52	11.1	3.54	4.67
IIm	0.82	3.1	1.59	4.51
		Polyamides (2)		
IVa	0.35	4.70	1.38	4.04
IVb	0.42	6.20	1.60	4.71
IVc	0.39	5.52	1.51	4.42
IVd	0.27	5.70	1.35	3.91
IVe	0.29	3.47	1.17	3.43
IVf	0.40	5.74	1.54	4.51
IVg	0.09	0.56	0.43	1.26
IVh	0.15	1.24	0.67	1.95
IVi	0.33	6.30	1.49	4.36
IVj	0.26	4.90	1.26	3.71
IVk	0.16	3.50	0.96	2.82
IVl	0.52	9.60	1.99	5.84
IVM	0.28	3.29	1.13	3.33
		Polyamides (3)		
IIa	0.41	5.10	2.23	4.37
IIb	0.42	6.20	2.40	4.71
IIc	0.50	8.20	2.79	5.47
IId	0.42	6.20	2.40	4.71
IIe	0.18	2.10	1.26	2.47

Table I (continued)

Polymer code	$[\eta]$	$\bar{M}_n.10^{-4}$	$r.10^7$	$(h^2)^{\frac{1}{2}}.10^7$
		Polyamides (4) "method A"		
Va	0.16	1.40	6.77	2.08
Vb	0.13	0.99	5.89	1.73
Vc	0.13	0.99	5.89	1.73
Vd	0.21	2.10	8.88	2.16
Ve	0.16	1.40	6.77	2.08
Vf	0.15	1.24	6.66	1.95
Vg	0.12	0.87	5.49	1.61
VIa	0.13	0.99	5.89	1.73
VIb	0.08	0.50	3.99	1.17
VIc	0.09	0.60	4.41	1.29
VId	0.14	1.11	6.27	1.84
VIe	0.11	0.80	5.19	1.52
VIf	0.10	0.70	4.81	1.41
VIg	0.07	0.40	3.54	1.04
		Polyamides (4) "method B"		
Va	0.26	2.93	1.06	3.12
Vb	0.35	4.66	1.37	4.03
Vc	0.18	1.65	0.78	2.28
Vd	0.20	1.94	0.85	2.49
Ve	0.32	4.05	1.27	3.73
Vf	0.26	2.93	1.06	3.12
Vg	-	-	-	-
VIa	0.08	0.46	0.39	1.14
VIb	0.18	1.65	0.78	2.28
VIc	0.25	2.75	1.03	3.02
VId	0.18	1.65	0.78	2.28
VIe	0.18	1.65	0.78	2.28
VIf	0.17	1.51	0.74	2.17
VIg	-	-	-	-

respectively, followed by catalytic reduction. Biphenyl-2,2'diyl and 1,1'-binaphthyl-2,2'diyl containing polyamides were obtained either by the direct polycondensation, method A,or low-temperature solution polycondensation of the diamines with aromatic dicarboxylic acid (or diacid chlorides), method B, (Scheme 4).

All the new polyamides **(1-4)** were previously prepared by the polycondensation method, and had high glass transition temperatures in the range 250 - 330 °C, and good thermal stability as well as excellent solubility in organic polar solvents such as NMP, N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO) and less polar as Py, and afforded transparent, almost amorphous and flexible films from the polymer solution. Thus, these aramides are considered to be promising soluble high temperature polymeric materials.

The viscosities for all the studied aramids solutions were measured at a concentration of 0.5 g/dl, in concentrated sulfuric acid at 30°C.

In addition the present work introduces some calculated polymeric parameters such as intrinsic viscosity, viscosity average molecular weight, end-to-end distance of the polymer chain, diffusion coefficients and excluded volume of the aramids at 30°C, and the interpretation of the data are discussed in the light of the recent theories and compared with other polymers.

RESULTS AND DISCUSSION

Determination of intrinsic viscosity $[\eta]$ by single specific viscosity measurement can be calculated from the Ram Mohan Rao and Yassen equation [13] by using the inherent viscosities (η_{inh}) for the studied polyamides [9-12].

The $[\eta]$ values obtained can be used to calculated the viscosity average molecular weight ($\bar{M}_n$) **(2 & 4)**, the radius (r) and the root-mean square end-to-end diatance $(h^2)^{3/2}$ of the polymer chain **(1-4)** by using the following relations;

$$[\eta] = K \bar{M}_n^a \qquad (1) \text{ Ref. [14]}$$

$$[\eta] = 10\pi Nr^3 / 3\bar{M}_n \qquad (2) \text{ ,, [15]}$$

$$[\eta] = \Phi (h^2)^{3/2} / \bar{M}_n \qquad (3) \text{ ,, [16]}$$

where K, a and Φ are constants, and N is the Avogadro's number.

It is found from the calculated $[\eta]$ values of the polyamides **(1-4)** that they are directly proportional to the $\bar{M}_n$ values as well as the radius which is determined, and the intrinsic viscosity is also related to the root-mean square end-to-end distance of the polymer chain.

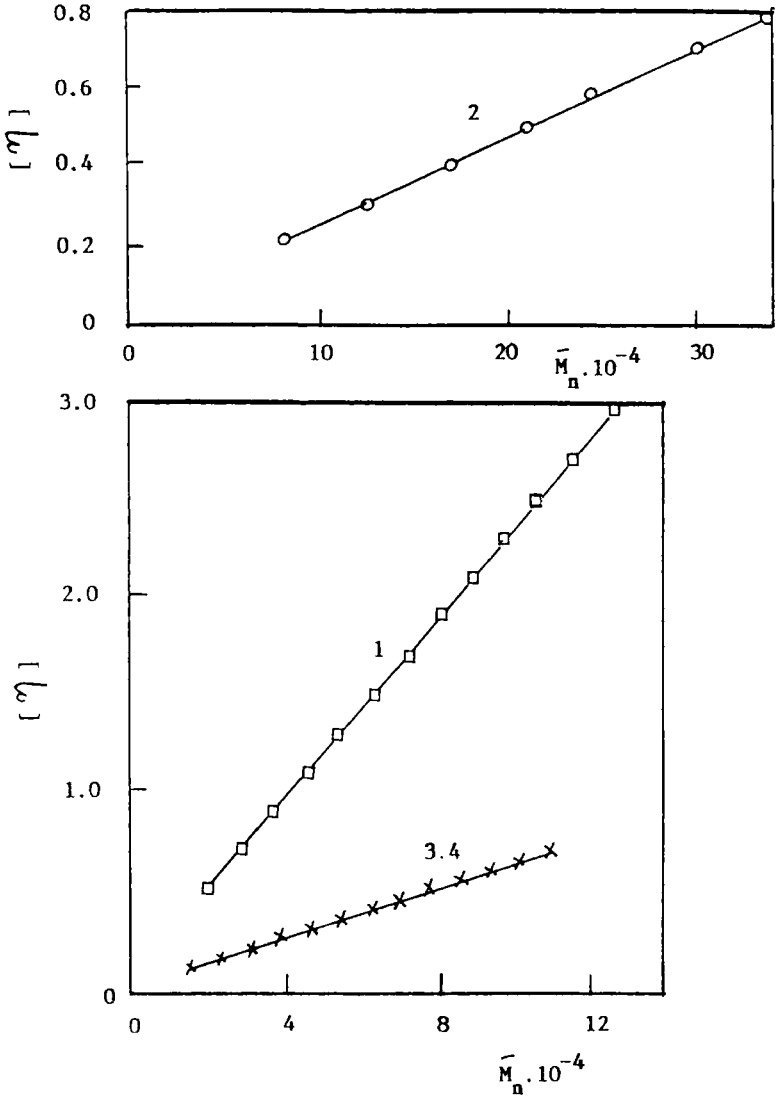


Fig. 1. $[\eta]$ vs, M_n for polyamides (1-4).

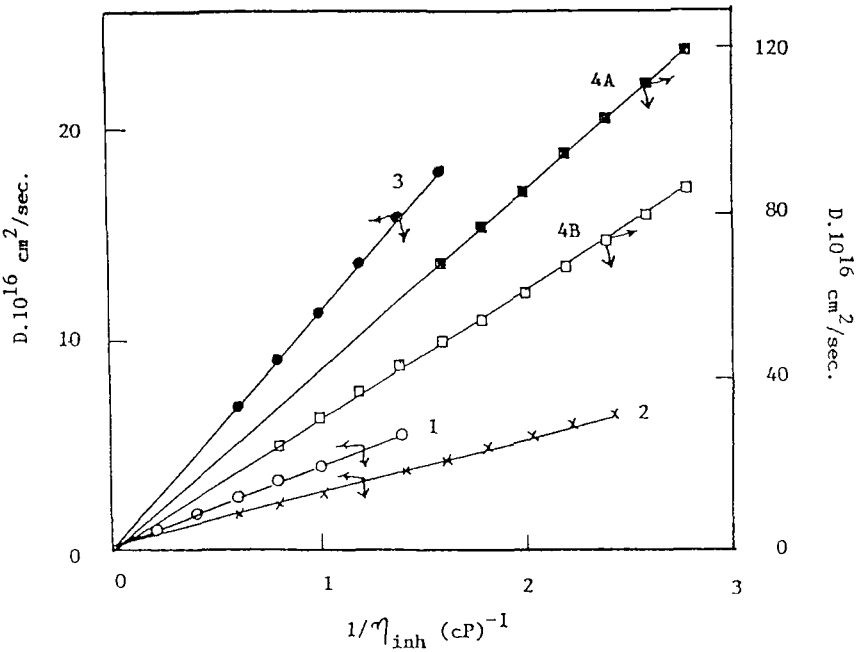


Fig. 2. D vs. $1/\eta_{inh}$ for polyamides (1-4)

Table I summarizes the calculated values of $[\eta]$, $\bar{M}_n$, r and $(h^2)^{\frac{1}{2}}$ for the studied polyamides. The linear least square plots of $[\eta]$ vs. M_n gave a straight lines (Fig. 1) which is a good agreement with polyarylates [17] and poly(nitroarylates) [18]. The observed $[\eta]$ - $(h^2)^{1/2}$ relationships for flexible polyamides molecules fall within the Flory-Fox theory [16].

Diffusion is directly connected with the molecular mobility, consequently, its rate should depend on their dimension. The quantitative relationship between the diffusion coefficient (D) and the size of a diffusion particle was obtained theoretically [15].

Figure 2, clearly shows that D - $1/\eta_{inh}$ relationship for all the polyamides (1-4), are linear which passes through the origin. This relationship suggests that the size of a polymer jumping unit is independent of the solvent and is polymeric specific, which explained the polymer-polymer solution interface, and in consistence with Zhang and Murray [19].

The mutual excluded volume of segments (B) for the flexible polyamides were determined [20]. The calculated values of $[\eta]/M^{\frac{1}{2}}$ are plotted against $M^{1/2}$ yeilding K as the ordinate intercept and B from

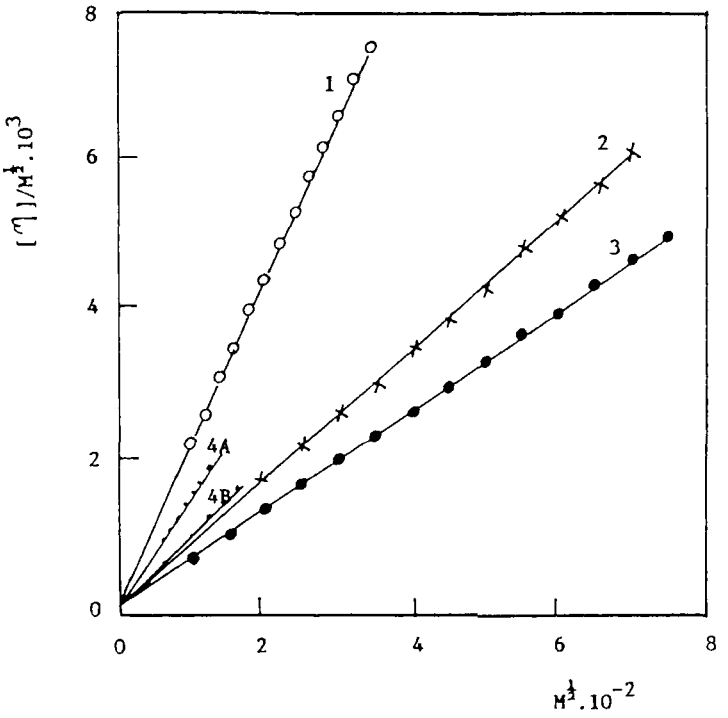


Fig. 3. $[\eta]/M^{\frac{1}{2}}$ vs $M^{\frac{1}{2}}$ for polyamides (1-4).

the slope (Fig. 3). It is found that the K values is equal to $5.0X10^{-6}$ for all the polyamides (1-4), and B values are tabulated as follows

Polymer no	1	2	3	4A	4B
$B.10^{28}$	1.74	0.69	0.53	1.24	0.77

The B values for all the studied polyamides gave almost the same results. This phenonena is considered to be due to the materials used (the various aromatic diamines with different aromatic acids) in the direct polycondensation method for the polyamides (1-4). The products had polymeric parameters included the Gaussian distribution characterizing the polymer in solution. Moreover, the mutual excluded volume is significantly smaller than the volume occupied by a polymer coil, i.e., $B \ll (h^2)^{3/2}$. For comparing the calculated B values of the polyamides (1-4) with other polymer values [21] , indicate that nonionic character for our polymers studied.

REFERENCES

1- P.Debye and A.M.Bueche, J. Chem. Phys., 16, 573 (1948).
2- J.G.Kirkwood and J.Riseman, ibid., 16, 505 (1948).
3- H.C.Brinkman, Applied Sci. Res., A1, 27 (1947).
4- W.Kuhn, Kolloid Z., 2, 68 (1934); W.Kuhn and H.Kuhn, Helv. Chim. Acta, 26, 1394 (1943); P.J.Flory, J. Chem. Phys., 13, 453 (1945).
5- G,L .Duda and J.S.Vrentas, J.S.Ju and H.T.Liu, ALChE J., 28(2), 279 (1982).
6- J.S.Vrentas and J.L.Duda, J. Appl. Polym. Sci., 22, 2325 (1978).
7- J.S. Vrentas, C.H.Chu, M.C.Drake and E.Von Meerwall, J. Polym. Sci. Polym. Phys., 27, 1179 (1989).
8- J.M.Zielinski and J.L.Duda, ALChE J., 38 (3), 405 (1992).
9- C.P.Yang, Y.Oishi, M.A.Kakimoto and Y.Imai, J. Polym. Sci. Part A, Polym. Chem., 27, 3895 (1989).
10- H.Manami and M.Nakazawa, J. Polym. Sci., Part A, Polym. Chem., 28, 465 (1990).
11- M.Xie, Y.Oishi, M.A.Kakimoto and Y.Imai, J. Polym. Sci., Part A, Polym. Chem., 29, 55 (1991).
12- G. S.Liou, Maruyama, M.A.Kakimoto and Y.Imai, J. Polym. Sci., Part A, Polym. Chem., 31, 2499 (1993).
13- M.V.Ram Mohan Rao and Yassen,J. Appl. Polym. Sci., 31,2501 (1986).
14- P.J.Flory, J. Am. Chem. Soc., 65, 372 (1943).
15- A.Einstein, Ann. Phys. (Leipzig), 19, 289 (1906); 34, 591 (1911).
16- P.J.Flory and T.G.Fox, J. Am. Chem. Soc., 73, 1904 (1951).
17- M.M.El-Banna, J. Pharm. Sci., Vol. 8(2), 109 (1994).
18- M.M.El-Banna, J. Macromol. Reports, A 31, 95 (1994).
19- H.Zhang and R.W.Murray, J. Am. Chem. Soc., 113, 5183 (1991).
20- W.H.Stockmayer and M.Fixman, J. Polym. Sci. Symp., 1, 137 (1963).
21- A.Takahashi and M.Nagasawa, J. Am. Chem. Soc., 86, 543 (1964).