

# Effect of Nature of Solvent on Viscosity of Poly-(methyl methacrylate) (PMMA)

<sup>1</sup>K. MAHMOOD\*, <sup>2</sup>A. SAEED AND <sup>1</sup>A. KHAN

<sup>1</sup>Chemistry Department, Gomal University,  
D.I.Khan, NWFP, Pakistan

<sup>2</sup>National Centre of Excellence in Physical Chemistry  
University of Peshawar, NWFP, Pakistan

(Received 23<sup>rd</sup> May, 2002, revised 6<sup>th</sup> February, 2003)

**Summary:** Poly(methyl methacrylate) (PMMA) samples of molecular weight  $6.49 \times 10^4$  -  $12.68 \times 10^4$  were investigated for their intrinsic viscosity, unperturbed chain dimension and chain expansion parameters in acetone and acetonitrile in the temperature range 10°- 40°C. Mark-Houwink's constants 'K' and 'a' are determined for the systems the data show that the  $\theta$  temperature for PMMA-Acetonitrile system is round about 35°C.  $K_\theta$  values have been predicted from various theoretical models and compared with experimental values, on the basis of which Ahmad-Baloch (AB) model is regarded as best for the theta solvent and Stockmayer-Fixman (SF) model for the good solvent. Using purely viscosity data radius of gyration ( $R_g$ ) and expansion factor ' $\alpha$ ' have also been calculated for both the systems and has been discussed.

## Introduction

In order to study the properties of a polymer one has to dissolve it in a suitable solvent, and apply various techniques, like light scattering, viscometry and osmometry. It is obvious that polymer behaves differently in different solvents, thus the concepts of good and poor solvent were introduced.

Among the various techniques, viscometry is one of the easiest and reliable methods for the

characterization of polymer samples. From the viscosity of the polymer solution one can get information about polymer-polymer and polymer-solvent interactions, on which the goodness of the solvent depends. Hydrodynamic volume, radius of gyration and other related informations can be obtained from the viscosity data. These parameters can also be determined by light scattering and osmometry techniques. In this paper we have tried

---

\*To whom all correspondence should be addressed.

purely viscosity data to obtain information about these parameters.

## Results and Discussion

### *Intrinsic viscosity*

From the flow times of solvent and solutions various viscosities were calculated according to equations 15-18. The relative and reduced viscosities show increase with concentration while inherent viscosity shows decrease with concentration. These are the usual trends. With increase in temperature all the viscosities show increase for the same concentration. This indicates the improving nature of the solvents with rise in temperature. To calculate the intrinsic viscosity, the data was treated further according to Huggin's equation [1].

$$\eta_{red} = \eta_{sp}/C = [\eta] + K_H [\eta]^2 C \quad (1)$$

The intrinsic viscosity was determined from the intercept of the plot of reduced viscosities vs. concentration; which are presented in figs. 1 and 2. These values are given in tables 1 and 2.

The values show an increase in intrinsic viscosity with temperature in both the solvents. This should be the case because intrinsic viscosity is the limiting value of reduced viscosity and as pointed out earlier the reduced viscosity shows increase with temperature. As the intrinsic viscosity is an index of the nature of the solvent, we can say that with increase in temperature the nature of the solvents improves.

### *Mark-Houwink Equation*

The intrinsic viscosity data was plotted against molecular weight according to Mark-Houwink equation [2], for the calculation of 'K' and 'a' values.

$$[\eta] = K M^a \quad (2)$$

The corresponding values of the constants are obtained from the intercept and slope of the plot of  $\log M$  vs.  $\log [\eta]$ , shown in fig. 3. On the basis of the above graph the following equations are suggested for PMMA-Acetone system,

$$[\eta]_{10} = 4.1574 \times 10^{-4} M^{0.57} \quad (3)$$

$$[\eta]_{15} = 4.1035 \times 10^{-4} M^{0.58} \quad (4)$$

Table-1: Molecular weight and intrinsic viscosity of PMMA in acetone.

PMMA SAMPLES	M.Wt $\times 10^{-4}$	INTRINSIC VISCOSITY (dl/g)				
		10 °C	15 °C	20 °C	25 °C	30 °C
UNF	12.68	0.341	0.386	0.439	0.484	0.556
Fr-I	27.16	0.542	0.589	0.657	0.743	0.836
Fr-II	26.28	0.532	0.569	0.612	0.692	0.788
Fr-III	9.69	0.300	0.318	0.365	0.388	0.455
Fr-IV	8.95	0.290	0.300	0.330	0.370	0.441
Fr-V	7.46	0.260	0.283	0.301	0.343	0.371
Fr-VI	6.49	0.236	0.254	0.278	0.310	0.339

UNF = Unfractionated, Fr = Fraction, M.Wt. = Molecular Weight.

Table 2: Molecular weight and intrinsic viscosity of PMMA in acetonitrile.

PMMA SAMPLES	M.Wt $\times 10^{-4}$	INTRINSIC VISCOSITY (dl/g)			
		30 °C	35 °C	40 °C	45 °C
UNF	12.68	0.106	0.178	0.223	0.290
Fr-I	27.16	0.150	0.237	0.295	0.376
Fr-II	26.28	0.150	0.231	0.287	0.366
Fr-III	9.69	0.094	0.140	0.173	0.220
Fr-IV	8.95	0.088	0.137	0.165	0.214
Fr-V	7.46	0.078	0.120	0.150	0.194
Fr-VI	6.49	0.076	0.117	0.148	0.174

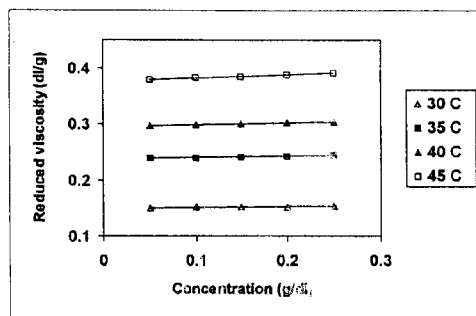


Fig. 1: Plot of reduced viscosity vs. concentration for PMMA (Fr-I) in acetonitrile at different temperatures.

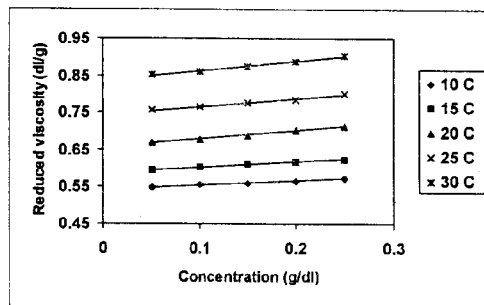


Fig. 2: Plot of reduced viscosity vs. concentration for PMMA (Fr-I) in acetone at different temperatures.

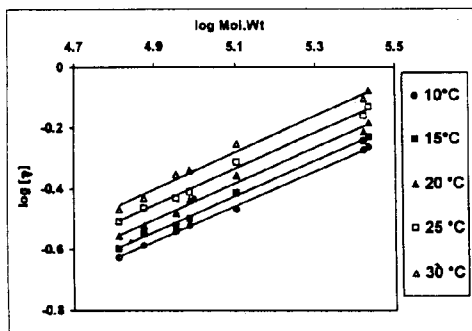


Fig. 3: log-log plot of intrinsic viscosity vs. molecular weight for PMMA in acetone.

$$[\eta]_{20} = 4.3935 \times 10^{-4} M^{0.58} \quad (5)$$

$$[\eta]_{25} = 4.3575 \times 10^{-4} M^{0.59} \quad (6)$$

$$[\eta]_{30} = 4.3926 \times 10^{-4} M^{0.60} \quad (7)$$

For PMMA-Acetonitrile system the following equations are proposed

$$[\eta]_{30} = 3.3282 \times 10^{-4} M^{0.48} \quad (8)$$

$$[\eta]_{35} = 4.3717 \times 10^{-4} M^{0.50} \quad (9)$$

$$[\eta]_{40} = 5.4825 \times 10^{-4} M^{0.50} \quad (10)$$

$$[\eta]_{45} = 5.5225 \times 10^{-4} M^{0.52} \quad (11)$$

From the results of the values of 'a', which is the index of the nature of the solvent, we can say that the nature of our solvents improve with temperature. Comparing the 'a' values of both the solvents, acetone is regarded as good solvent. In case of acetonitrile its nature improves from poor to good passing through theta condition.

Another test for the nature of the solvent is to plot  $\log [\eta]/M^{1/2}$  vs.  $\log M$ , (fig. 4), [3], it can be seen that in case of acetonitrile the data regarding  $\log [\eta]/M^{1/2}$  show no dependency on molecular weight which is the characteristic of theta solvent, while in case of acetone (good solvent), the dependency is prominent.

#### Unperturbed chain dimension

Various theoretical predictions [4-9] have been used for the estimation of unperturbed chain

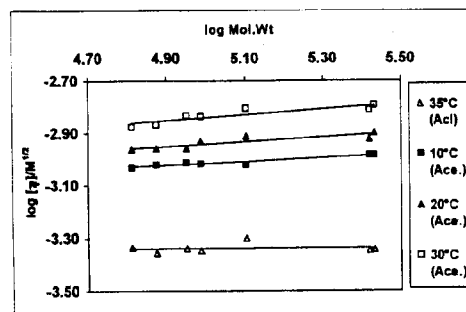


Fig. 4: Double log graph of  $[\eta]/M^{1/2}$  vs. Mol. Wt for PMMA in acetonitrile and acetone at different temperatures.

Table 3: Values of  $K_0$  ( $\times 10^4$ ) for PMMA in acetone from different theoretical equations.

Equation	10°C	15°C	20°C	25°C	30°C
FF	8.197	8.732	9.667	10.451	11.820
KS	8.353	8.904	9.790	10.662	12.001
B	8.221	8.760	9.704	10.493	11.864
SF	8.384	8.937	9.805	10.695	12.030
ISK	10.416	11.018	11.979	12.950	14.405
AB	5.798	6.360	7.240	8.119	9.609

Table 4: Values of  $K_0$  ( $\times 10^4$ ) for PMMA in acetonitrile from different theoretical equations.

Equation	30°C	35°C	40°C	45°C
FF	3.020	4.664	5.797	7.208
KS	3.016	4.616	5.721	7.064
B	3.020	4.663	5.795	7.204
SF	3.014	4.593	5.684	6.996
ISK	4.120	6.182	7.647	9.225
AB	1.437	2.330	2.884	3.861
Experimental	3.379	4.393	5.422	5.456

dimension of PMMA in both the solvents. From the Mark-Houwink relationships for acetonitrile we can say that the theta temperature lies between 30° and 35°C and the value of the constant 'K' in equation 9 can be considered as  $K_0$ . This value will be compared with the values obtained from other equations [4-9]. Comparing values of  $K_0$  (tables 3-4) obtained by different theoretical predictions, figs. 5-8, it is observed that in case of good solvent the Ahmad-Baloch (AB) model gives values closer, though higher, than the experimental value. In case of PMMA-acetonitrile system similar values of  $K_0$  are obtained from different models except that proposed by Ahmad and Baloch. The Inagaki-Suzuki-Kurata (ISK) model gives unexpected higher values of  $K_0$  in both the systems. The variation in  $K_0$  values in case of A-B model may be attributed to a different approach adopted in their model. These authors have

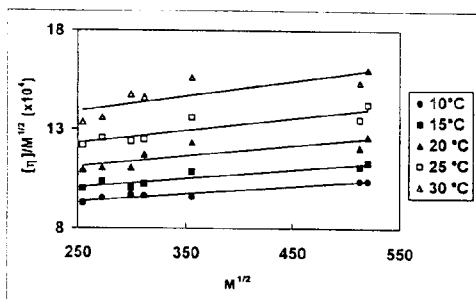


Fig. 5: Graph of Stockmayer-Fixman equation for PMMA in acetone,  $\{[\eta]/M^{1/2} = 0.51 \phi_0 BM^{1/2}\}$

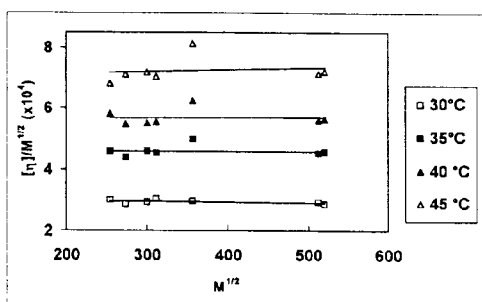


Fig. 6: Graph of Stockmayer-Fixman (SF) equation for PMMA in acetonitrile.

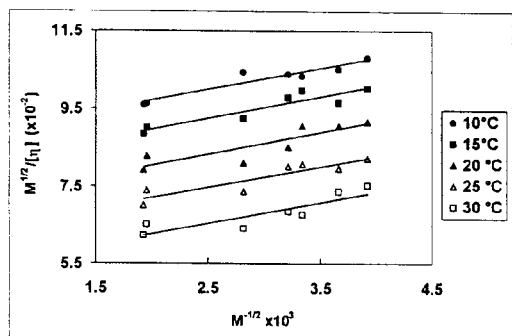


Fig. 7: Graph of Ahmad-Baloch equation for PMMA in acetone  $\{M^{1/2}/[\eta] = \frac{1}{2} K_\theta + (0.908/\Phi_0)^{1/3} r_0 K_\theta^{2/3} M^{1/2}\}$ .

used hydrodynamic radius ' $r_h$ ' instead of interaction parameter ' $B$ ' which is equivalent to second virial coefficient ' $A_2$ '. Variation in hydrodynamic radius with molecular weight is different as compared to  $A_2$  and this difference is reflected in the different values of  $K_\theta$ . Our values of  $K_\theta$  and also of literature [10-11] show that different  $K_\theta$  values are obtained for different solvents, which is in contradiction to the

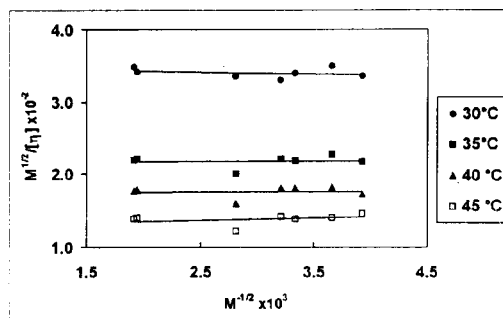


Fig. 8: Graph of Ahmad-Baloch (AB) equation for PMMA in acetonitrile.

theoretical prediction. This may be because the theories do not consider the chemical nature of the solvent, which lead to specific interaction between the given polymer-solvent pair. Thus the specific interaction between the polymer and solvent are also important and should be taken into consideration.

From the values of  $K_\theta$  the unperturbed chain dimension ' $R_g$ ' was calculated by the well known Flory-Fox equation [2], i.e.

$$R_g = \frac{1}{6} \left[ \left( \frac{K_\theta}{\Phi} \right)^{2/3} M \right]^{1/2} \quad (12)$$

Where  $\Phi$  is a universal constant, being equal to  $2.5 \times 10^{21} \text{ mol}^{-1}$  [12],

There results are shown in tables 5 and 6. The results are different from that of Abe *et al.*, [3], who determined the  $R_g$  values from the light scattering method on samples of different molecular weights.

#### Chain expansion parameter

In theta solvent the polymer molecules are in the unperturbed state, while in case of acetone, a good solvent, the chains are swollen and inter and intra chain interactions play their part. To examine the effect of the solvent, a chain expansion parameter is defined as

$$\alpha_\eta^3 = [\eta]/[\eta_\theta] \quad (13)$$

According to theoretical prediction [13] the molecular weight dependence of  $\alpha_\eta$  follow the relationship

Table 5: Root mean square radius of gyration ( $R_g$ , Å) for various fractions of PMMA in acetonitrile (Acl) and in acetone using SF equation.

Fractions	Experimental (35°C, Acl)	40°C (Acl)	45°C (Acl)	25°C (Acetone)
UNF	33.24	36.22	38.82	44.72
FR-I	48.65	53.01	56.81	65.44
FR-II	47.86	52.15	55.89	64.38
FR-III	29.07	31.67	33.94	39.10
FR-IV	27.92	30.43	32.61	37.56
FR-V	25.50	27.79	29.78	34.30
FR-VI	23.78	25.91	27.77	31.99

Table 6: Root mean square radius of gyration ( $R_g$ , Å) for various fractions of PMMA in acetonitrile (Acl) and in acetone using AB equation.

Fractions	Experimental (35°C, Acl)	40°C (Acl)	45°C (Acl)	25°C (Acetone)
UNF	33.24	28.89	31.84	40.79
FR-I	48.65	42.28	46.60	59.70
FR-II	47.86	41.60	45.84	58.73
FR-III	29.07	25.26	27.84	35.67
FR-IV	27.92	24.27	26.75	34.27
FR-V	25.50	22.16	24.42	31.29
FR-VI	23.78	20.67	22.78	29.18

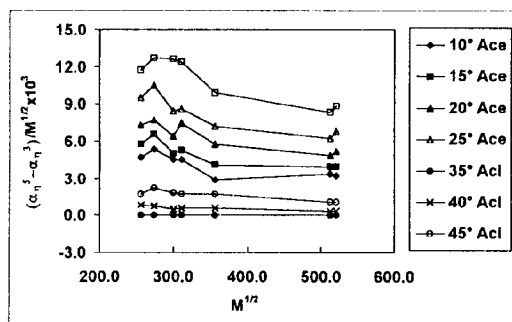


Fig. 9: Graph plotted according to equation 14 for PMMA in acetone and in acetonitrile at different temperatures.

$$\alpha_n^5 - \alpha_n^3 = C_n B_0 g (R_g^2/M)^{-3/2} M^{1/2} \quad (14)$$

Where  $C_n$  is constant and  $g$  is a function of  $(1-\theta/T)$  but may not always be linear to  $(1-\theta/T)$ .

Equation 14 predicts constant values for  $(\alpha_n^5 - \alpha_n^3)/M^{1/2}$  when plotted against  $M^{1/2}$  but we can see from the fig. 9, that the consistency is some how observed in case of acetonitrile particularly at and near  $\theta$  temperature but in case of acetone the data show different behavior. A similar behavior has also been observed in other cases [14]. The deviation may

be due to low molecular weight ranges used and partial draining in the polymer coil dissolved in good solvent.

### Experimental

The materials used were PMMA from BDH Co. and the solvents, acetone and acetonitrile, were from Merck Co. and BDH Co. respectively.

Fractionation of the polymer was carried out in acetone using ethanol as non-solvent. Solutions of PMMA samples (fractionated as well as unfractionated) in both the solvents (acetone and acetonitrile) were prepared in the concentration range 0.05 to 0.25g/dl. Canon Fanske viscometer was used for measurement of flow times of solutions, in the temperature range 10-30 °C for acetone and 30-45 °C for acetonitrile. Water bath from F.G. Bood & Co. Germany, was used.

From the flow times the various viscosities were calculated according to the equations,

$$\eta_{rel} = \eta/\eta_0 \quad (15)$$

$$\eta_{red} = (\eta_{rel} - 1)/C \quad (16)$$

$$\eta_{inh} = (\ln \eta_{rel})/C \quad (17)$$

$$[\eta] = (\eta_{red} \text{ or } \eta_{inh}) \text{ Limit } C \rightarrow 0 \quad (18)$$

Where  $\eta$  and  $\eta_0$  are solution and solvent viscosities respectively,  $\eta_{rel}$  = relative viscosity,  $\eta_{red}$  = reduced viscosity,  $\eta_{inh}$  = inherent viscosity,  $[\eta]$  = intrinsic viscosity (reduced or inherent viscosity when concentration approaches to zero) and  $C$  = concentration.

### References

1. M.L. Huggin, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
2. Jan F. Rabek, "Experimental Methods in Polymer Chemistry", John Wiley and Sons New York (1990)
3. F.Abe, K. Horita, Y. Einaga and H.Yamakawa, *Macromolecules*, **27**, 725 (1994).
4. P.J. Flory and T.G. Fox, *J. Am. Chem. Soc.*, **37**, 1904 (1951).
5. M. Kurata, and W.H. Stockmayer, *Fortschr. Hochpolymer Forsch*, **3**, 196 (1963).

6. G.C. Berry, *J. Chem. Phys.*, **16**, 1338 (1967).
7. W.H. Stockmayer and M. Fixman, *J. Polym. Sci. Part C*, **1**, 137 (1963).
8. H. Inagaki, H. Suzuki and M. Kurata, *J. Polym. Sci.*, **C15**, 409 (1966)
9. N. Ahmad and M.K. Baloch, *J. Macromol. Sci. Chem.*, **24(10)**, 1241 (1987).
10. M. K. Baloch, *polymer Bulletin*, **25**, 245 (1991).
11. O. Qudrat and L. Mrkvicova, *Europ. Ploymer. J.*, **17**, 1155 (1981).
12. Y. Miyaki, H. Fujita and M. Fukuda, *Macromolucules*, **14**, 210 (1981)
13. H. Fujita, *Polymer Solutions*, Elsevier Science Publishers, New York (1990).
14. I. Noda, K. Mizutani and T. Kato, *Macromolecules*, **3**, 787 (1970).