Light ScatteRing Studies of Poly(methyl methacrylate) (PMMA) in Different Solvents

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Summery:Unfractionated and fractionated samples of poly(methyl methacrylate) (PMMA) were characterized by static light scattering (SLS) and gel permeation chromatography GPC) techniques at room temperature (33°C) in acetone and acetonitrile. Our result showed that the samples did not show any angular dependency. From static light scattering (Turbidity) measurements molecular weight (M_w) and second virial coefficient (A_2) were determined. The positive values of A_2 in case of acetone show that acetone is good solvent for PMMA while the A_2 values for acetonitrile show that acetonitrile is a theta solvent. The light scattering results are in consistent to that of GPC results, (conducted at Aberdeen University UK).

Introduction

Polymers have high molecular weights ranging from thousands to millions [1]. Due to this high molecular weights, this class of compounds show properties not shown by low molecular weights compounds. Molecular weights is important while discussing the properties of the polymers. It is used, (i) in Mark-Houwink's equation [2] i.e.

$$[\eta] = KM^{\alpha} \qquad (1)$$

for the determination of K and α,

(ii) for the determination of K_θ from various theoretical equations [3-7], e.g.

$$\frac{[\eta]}{M^{1/2}} = K_\Theta + 0.51\Phi BM^{1/2} \qquad (2)$$

and (iii) the Flory equation [2]

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

for the calculation of dimensions of the polymer molecules.

Where [η]= Intrinsic viscosity, M= Molecular weight, R_g = Radius of gyration, Φ= Flory's constant,α, K and K_Θ are constants for the system.

Molecular weights may be number average (M_n) or weight average (M_w) [8] and different methods are employed for their determination e.g. osmotic pressure, cryoscopy, ebullioscopy and end group analysis methods are among those used for M_n determination while light scattering and ultra centrifugation methods are used for M_w. Further polymers show distribution in molecular weights. To get samples of narrowly distributed molecular weights, fractionation methods are employed among which gel permeation chromatography (GPC) [1] and precipitation methods [9] are commonly used.

We know that polymers behave differently in different solvents and on this basis the solvents are classified as good, bad or theta solvents. Depending on the values of α of equation (1) and of second virial coefficient (A_2), the nature of the solvent can be judged.

In the series of experimental work on dilute solution properties of PMMA, viscometric study and size determination has already been discussed [10]. Present paper deal with determination of molecular weight and second virial coefficient, using static light method.

Results and Discussion

Following the experimental procedure HC/τ values for all the fractions were determined. According to equation (4) these values of HC/τ were

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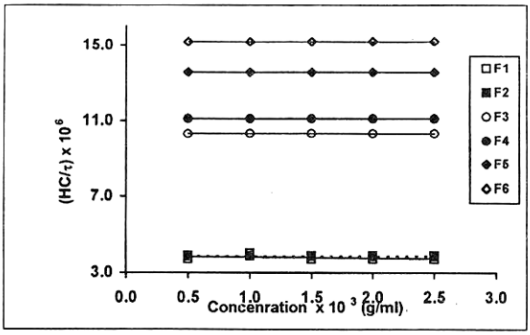


Fig. 1: Turbidity vs. concentration for various fractions of PMMA in acetonitrile.

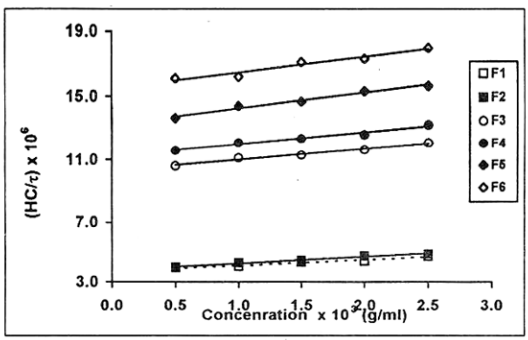


Fig. 2: Turbidity vs. concentration for various fractions of PMMA in acetone.

plotted against concentration (C) figs. 1 and 2. M_w and A_2 were calculated from the intercept and slope of the curve respectively. The corresponding values are given in table-1. The molecular weights and A_2 values at both the wavelengths (436nm and 536nm) are in close agreement with each other and the reported values in table-1 are the average values. The positive values of A_2 in case of acetone show that acetone is a good solvent for PMMA while the decrease of A_2 with the increase in M_w shows that the solvent quality become poor as the M_w increases. Other researchers also report this trend, for PMMA [11-14] and for other polymers [15-17].

The A_2 values in case of acetonitrile shows that acetonitrile is a theta solvent for PMMA at 33°C. The findings of other researcher are that theta temperature for acetonitrile is 30°C [18], 27.6°C [19] and 48°C [20].

Table 1: Molecular weight (M_w) and second virial coefficient (A_2) (cm^3 Mol g^{-2}) values of PMMA samples in acetone

PMMA	ACETONE		ACETONITRILE	
Samples	$M_w x10^{-4}$	$A_2 x10^4$	$M_w x10^{-4}$	$A_2 x10^6$
FI	27.25	1.99	27.09	0.69
FII	26.48	2.60	26.12	0.93
UNF	12.69	3.08	12.66	-0.22
FIII	9.74	3.53	9.71	0.38
FIV	8.88	4.01	9.01	-1.28
F V	7.49	4.79	7.45	-1.24
F VI	6.48	5.11	6.48	4.08

Table 2: Analysis report of PMMA samples by gel permeation chromatography (GPC)

SAMPLES	$M_w x10^{-4}$	$M_n x10^{-4}$	$n = M_w/M_n$
FI	27.10	14.86	1.82
FII	26.22	16.85	1.55
FIII	9.63	5.02	1.92
FIV	8.95	6.19	1.45
F V	7.43	5.09	1.46
F VI	6.51	5.16	1.26

Table 3: Average molecular weights from light scattering and GPC

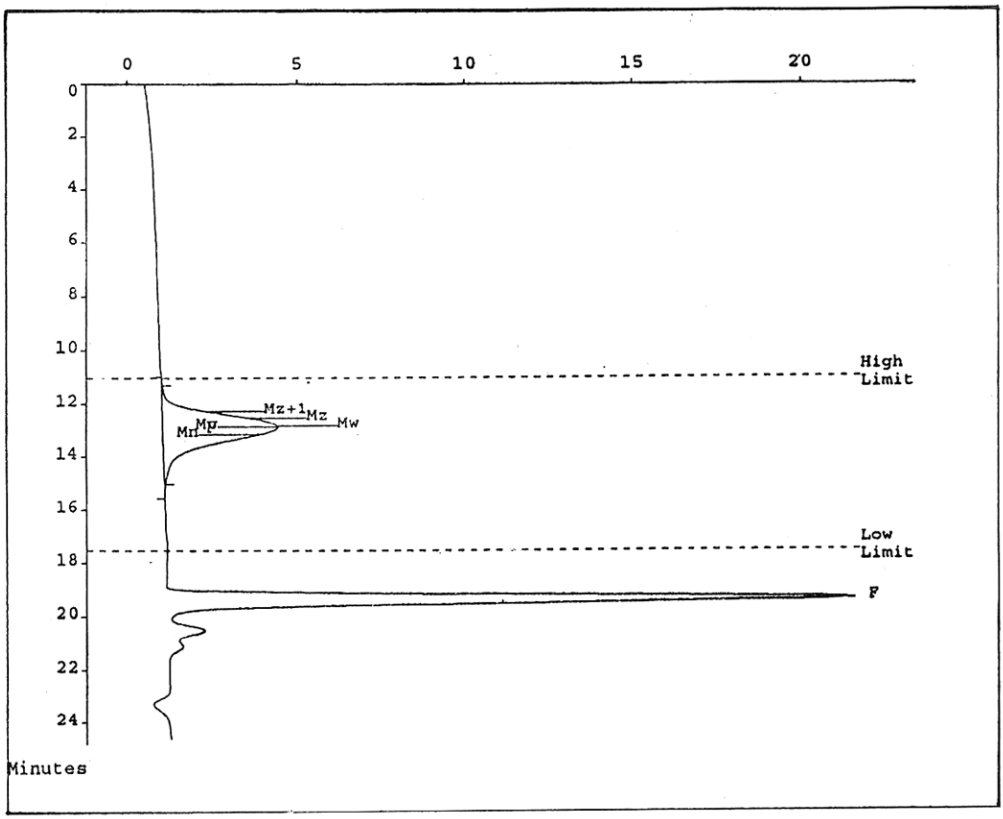
SAMPLES	$M_w x10^{-4}$
FI	27.16
FII	26.28
UNF	12.68
FIII	9.69
FIV	8.95
F V	7.46
F VI	6.49

For comparison the GPC results are given in Table-2, which are consistent with light scattering results, Fig. 3 show the GPC spectrum for fraction II (FII). The naverage values of the molecular weight of the polymer samples from all the techniques i.e. GPC and light scattering at two wave lengths are presented in Table-3.

Fig. 4 shows a double logarithmic plot of A_2 vs. M_w for the PMMA fractions in acetone drawn according to the following equation

$$A_2 = KM^{-\alpha} \quad (7)$$

K and α values, as calculated from the intercept and slope of the curve are 0.45 and –0.61 respectively. The exponent values is higher that 0.25, predicted for typical random-coil polymer chains



Molecular Weight Averages

Mp =	244728	Mz =	378430
Mn =	168556	Mz+1 =	533734
Mw =	262186	Mv =	247303
Polydispersity =	1.555	Peak Area =	49197

Fig. 3: GPC Spectrum for PMMA fraction II (F II)

[21], which may reflect that PMMA have a more extended chain conformation in acetone at 33°C. As pointed out by Springer *et al* [14] plots of log A_2 vs. log M over a wide range of M follow a curve which is convex downward slightly. The same trend can be seen in fig. 4. Thus in principal the 'α' is not constant but decreases with increasing M, but this decrease is so small that α can be taken as constant.

Experimental

Unfractionated and fractionated samples of poly(methyl methacrylate) (PMMA) (BDH Co.) of unknown molecular weights were characterized by static light scattering technique at 33°C in two solvents, acetone (Merck Co. Germany) and acetonitrile (BDH).

For solution preparations acetone and acetonitrile were used without further purification. For each fraction, five solutions, in the range of $5x10^{-4}$ – $2.5x10^{-3}$ g/mL, were prepared by dilution method. All solutions were filtered at room temperature using Whatman filter, depending on the polymer size. For fractionation purpose acetone was used as solvent and methyl alcohol as non-solvent [22]

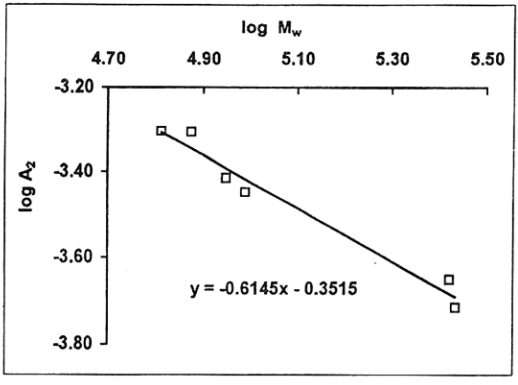


Fig. 4: Double logarithmic plot of second virial coefficient (A_2) and molecular weight (M_w) in acetone.

Light Scattering Measurements

A commercial light-scattering Photometer of Brice Phoenix Co. USA was used for light scattering studies. The photometer was calibrated with standard/ toluene to make sure that the scattering intensity from toluene has no angular dependence in the angular range of 20° – 150°. The detail of the light scattering instrumentation and theory can be found in its manual [23]. All light scattering measurements were done at 33°C. In static light scattering, the following equation has been used.

$$HC/\tau = 1/M + 2\,A_2\,C \qquad (4)$$

Where $$H = 32\,\pi^2\,n^2 / 3\,N\lambda^4\,(\delta n/\delta C)^2 \qquad (5)$$

With λ= wavelengths used i.e. 436nm & 546nm, N = 6.023 x 10^{23}, n = Refractive index of the solution. $\delta n/\delta C$ = Refractive index increment (literature values were used) [24]

0.136 (436nm) & 0.134 (546nm) for acetone,

0.140 (436nm) & 0.137 (546nm) for acetonitrile

$$\tau = \left[\frac{16 T_D\, a}{3(1.049)h}\right] n^2 \left(\frac{R_w}{R_C}\right) F \frac{D_S}{D_W} \qquad (6)$$

R_W/R_C is a solvent dependent parameter and was determined experimentally, $F(D_S/D_W)$ is solution dependent parameter with D_S, D_w = scattering values at 90° and at 0° respectively (with respect to incident light) with proper combination of filters 'F'. Values in the brackets are all constants for the instrument and 'n' = refractive indices of the solvents.

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