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### Flow Behaviour of Concentrated Solutions of Poly(Methyl Methacrylate)

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**Summary:** The flow behaviour of unfractionated poly(methyl methacrylate) (PMMA) ( $M_w = 1.27 \times 10^5$ ) in acetone and acetonitrile was studied in concentration range 2-12 gm/dl with 2gm/dl increment, in the temperature range 10-30°C for acetone and 30-45°C for acetonitrile with 5°C interval. Roto-viscometer with NV sensor system was used for this purpose. From the data it was observed that three distinct regions could be seen in shear viscosity ( $\eta$ ) as the shear rate ( $\dot{\gamma}$ ) was varied from 2.7-245 s<sup>-1</sup>. The viscosity was almost constant in the low and high shear rate regions, while in the shear rate region 12-244s<sup>-1</sup> viscosity showed a decrease. The zero shear viscosities were calculated by taking the average of first three readings. From this data the critical concentration ( $C^*$ ), where entanglement occurred, was shown to be above 6 gm/dl.

#### Introduction

Numerous experimental studies have been conducted on dilute solution properties of various polymers. Less attention has been given to study the properties (especially the flow properties) of concentrated polymer solution.

In dilute solutions especially in good solvents, the polymer molecules are fully expanded [1]. As the concentration increases, the coil contracts due to the excluded volume effects between segments in the same chain and at very high concentration the molecular dimension remain unaffected by the nature of the solvent and reach to unperturbed value [2].

Concentrated solutions show different flow behaviour than dilute solutions and very important informations like zero shear viscosity [3], effect of shear rate and shear stress on viscosity and other related information can be obtained from such studies, which are useful in polymer processing operations M Saleem [4] studied the rheological

behaviour of PVA in cyclohexane, while Ali Khan [5] conducted the same studies on polystyrene in tetrahydrofuran (THF). Both the researchers found a drastic decrease in shear viscosity as the shear rate was increased. As far as the authors know no such studies have been conducted on PMMA, so the experiments were conducted to observe the flow behaviour of concentrated PMMA solutions in acetone (good solvent) and acetonitrile (theta solvent).

#### Results and Discussion

The viscosity of most the fluids does not change with the shear rate but some systems, like polymer solutions, show variation in viscosity values with shear rate. The former class of substances are called Newtonian Fluids while the later class of substances are said to exhibit non-Newtonian behaviour. The viscosity of such systems are studied in specially designed viscometers. One of the such type used by us was Roto Viscometer, the details of which are given in experimental section.

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Following the experimental techniques [6], the data obtained is discussed here. Using equations 1 and 2, the shear rate ( $\dot{\gamma}$ ) and shear viscosities ( $\eta$ ) were calculated, some of which are presented in Table 1-2. To see the behaviour of the solution at different shear rates, the graphical representation is given in figures 1,2. Here the Ln viscosity ( $\text{Ln } \eta$ ) is plotted against Ln shear rate ( $\text{Ln } \dot{\gamma}$ ). Almost all the graphs show similar behaviour that is:

- I. Viscosity is almost independent of shear rate in the low shear rate region ( $n = 2.7\text{s}^{-1}$  to  $12\text{s}^{-1}$ ), where  $\text{s}^{-1}$  represent revolutions per second.
- II. Decrease takes place in viscosity with increase in shear rate in the region  $12\text{s}^{-1}$  to  $244\text{s}^{-1}$ .
- III. At higher shear rate ( $\dot{\gamma} > 244\text{s}^{-1}$ ) the viscosity seems to be less dependent on shear rate.

Table-1: Shear rate and shear viscosities for PMMA(UNF.) in acetonitrile at 45°C for different concentrations

S.Rate (Sec <sup>-1</sup> )	2%	4%	6%	8%	10%	12%
5.41	16.45	24.09	32.90	49.35	82.25	131.60
10.82	16.45	22.74	32.90	49.35	82.25	131.60
21.64	16.45	22.74	28.79	42.97	82.25	131.60
43.28	12.34	22.74	28.70	49.35	69.91	111.04
86.56	10.28	18.61	16.65	29.81	63.26	102.04
173.12	6.51	8.23	11.18	24.23	60.78	102.04
346.23	5.14	7.37	10.67	26.86	55.77	89.44
692.49	4.34	6.68	10.28	22.33	47.81	89.44
1384.92	4.20	6.36	9.22	24.33	44.40	82.47
2769.99	4.11	6.15	8.23	21.37	40.76	80.32

Table-2: Shear rate and shear viscosities for PMMA(UNF.) in acetone at 25°C for different concentrations

S.Rate (Sec <sup>-1</sup> )	2%	4%	6%	8%	10%	12%
5.41	26.45	31.64	42.90	64.78	75.80	108.70
10.82	26.45	31.64	42.90	61.15	74.44	100.48
21.64	23.56	29.26	38.79	64.78	72.51	96.37
43.28	22.77	29.26	42.90	55.96	72.72	98.42
86.56	17.38	20.82	39.70	39.70	44.56	92.25
173.12	17.20	20.82	30.69	36.39	50.61	85.57
346.23	15.63	17.45	28.51	36.22	50.61	76.83
692.49	14.88	17.07	21.07	37.93	45.56	68.60
1384.92	14.88	16.81	21.07	30.18	42.34	67.25
2769.99	14.63	16.81	21.07	30.18	42.34	65.11

This means that polymer show a non-Newtonian behaviour, during flow for semidilute and concentrated solution. The change in the viscosity in the middle portion of the curves may be due to the following two reasons [5].

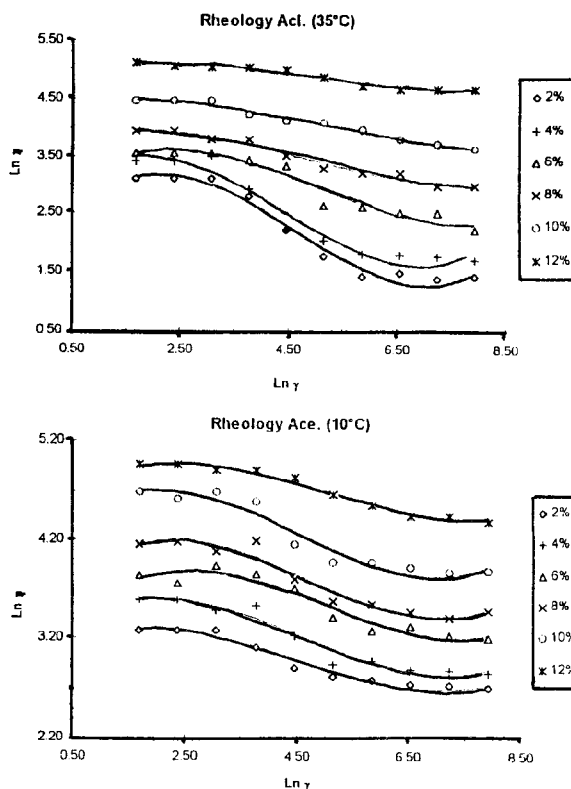


Fig. 1: Double logarithmic graphs of shear viscosity ( $\eta$ ) vs. shear rate ( $\dot{\gamma}$ ) for PMMA in acetonitrile at 35°C and acetone at 10°C.

- I. That the solutions have loosely bound association of macromolecules, which when subjected to shear, open up quickly resulting in the decrease in the shear viscosity.
- II The decrease in viscosity may also be due to orientation of molecule along the flow direction. When the molecules completely orient themselves along the flow, then the viscosity become least dependent on shear rate.

The graphs also show that the effect of shear rate on viscosity in the shear rate range  $12\text{s}^{-1}$  to  $240\text{s}^{-1}$  is more pronounced at lower concentration (2 - 6 g/dl) as compared to the relatively high concentrated solutions (above 6 g/dl). This indicate that at lower concentrations, low shear rates are enough to orient the molecules in the direction of shear. When the concentration increases, chain

entanglement occurs and thus a network is formed. The presence of this network hinders the alignment of molecules along the direction of shear and therefore no pronounced effect of the rate of shear is observed for these concentrations (8-12 g/dl).

It may be seen from the graphs that the shear viscosities increase with concentration which is a natural phenomena. With increase in concentration the solutions become more and more viscous, the interactions between polymer-polymer and solvent-polymer increase [7], resulting in the higher values of the viscosities. This trend is shown by all the solutions at each temperature. Comparing the viscosities at different temperatures, it can be seen that within experimental errors, the viscosity decrease with temperature although the decrease is not linear. The temperature effect can be attributed to the breaking down of supermolecular structure [8] and increase in the spacing of coupling entanglement [9].

Scanning the data (Table 1-2) and graphs (Fig. 1) of shear viscosities and shear rate for polymer solution in both the solvents one can observe the same trend in the data. Acetone is good solvent than acetonitrile, but no prominent change in the values of shear viscosity can be observed, which may be due to the higher concentration of the solutions [2].

#### Zero shear viscosity

The zero shear viscosity can be obtained from extrapolation of the graph to zero shear rate. We have calculated zero shear viscosity by averaging the first three readings of the shear viscosity. The values are given in Table 3,4 for acetonitrile and acetone respectively. The zero shear viscosity is a measure of energy dissipation and is a parameter describing the rheological properties of polymer solution and melts in the region of deformation [10]. Zero shear viscosity is a complex function of concentration and temperature of the polymer solution and molecular weight of the polymer used.

Variation in zero shear viscosity with concentration and temperature are presented graphically in figure 2 and 3. Zero shear viscosity, in a way, is a check for the thermodynamic quality of the solvent, because when polymer is dissolved in a

Table-3: Zero shear viscosities for PMMA (UNF.) in acetonitrile at different concentrations (gm/dl)

Temp.(K)	2%	4%	6%	8%	10%	12%
303.0	22.98	32.21	46.59	58.69	92.63	196.02
308.0	22.08	31.37	35.18	48.89	85.67	157.56
313.0	16.45	23.03	34.21	49.94	82.24	142.42
318.0	16.45	23.18	31.47	47.12	82.25	131.60

Table-4: Zero shear viscosities for PMMA (UNF.) in acetone at different concentrations (gm/dl)

Temp.(K)	2%	4%	6%	8%	10%	12%
283.0	26.45	34.67	46.67	62.59	105.34	138.81
288.0	27.22	33.71	41.09	61.97	83.10	121.07
293.0	27.72	30.84	41.78	59.66	75.40	107.31
298.0	25.45	30.83	41.48	63.54	74.24	101.72
303.0	23.62	25.47	33.53	42.39	55.19	96.18

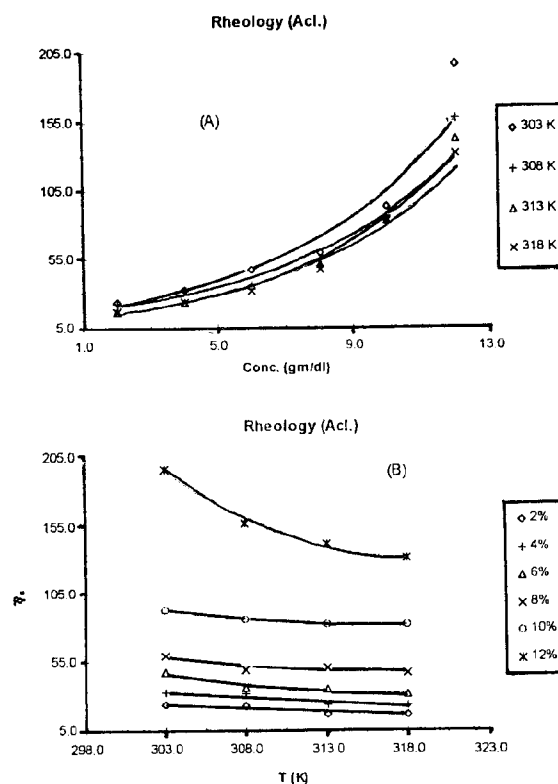


Fig. 2: Graphs of zero shear viscosity ( $\eta_0$ ) vs. concentration (A) and vs. Temperature (B) for PMMA (UNF.) in acetonitrile.

solvent, molecules have random orientations, depending on the solute-solute and solute-solvent interactions. When the system is sheared, as discussed earlier, the orientation changes, which in turns changes the extent of entanglement and hence

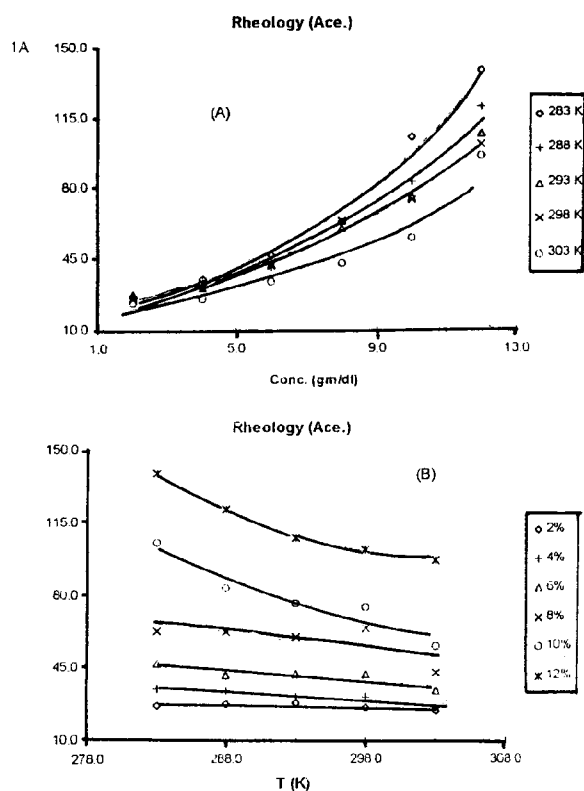


Fig. 3: Graphs of zero shear viscosity ( $\eta_0$ ) vs. concentration (A) and vs. Temperature (B) for PMMA (UNF) in acetone.

the viscosity which can be seen from figure 2A and 3A, showing the variation of zero shear viscosities with concentration. The trend is not linear, zero shear viscosity first increase slowly and then abruptly. This abrupt increases in viscosity can be attributed to entanglement of molecules [11-13], which is not present at low concentration. So this trend shows a critical concentration region (lying between 6% and 8%) above which the behaviour of the system changes. The increased activation energy of flow [14] also explains the high viscosity for the system. With increased concentration, more energy is required for flow and so the zero shear viscosity.

Figures 2B and 3B show the variation of zero shear viscosity with temperature. These graphs, show that zero shear viscosity decreases with temperature, but the variation pattern is different for different concentrations. At low concentration the

temperature effect is low, while for highly concentrated solutions the effect is greater. In case of acetone, in the lower concentration range, zero shear viscosity first seems to increase and then decrease. The probable reason for this may be the entanglement effect. First due to entanglement of molecules, the zero shear viscosity increases with temperature, but at higher temperature the activation energy dominates the entanglement effect and so as a whole the viscosity decreases.

### Experimental

Unfractionated and uncharacterized sample of PMMA ( $M_w = 1.27 \times 10^5$ ) from BDH Co. were studied in two solvents acetone and acetonitrile. The concentration range used was between 2-12 gm/dl with 2 gm/dl increment, in the temperature range 10-30°C for acetone and 30-45°C for acetonitrile with 5°C interval. The PMMA sample was dried in oven between 59-60°C before using. HAAKE-RV12-ROTARY-VISCOMETER of Germany with NV sensor system was used for viscosity measurement. The temperature was controlled with the help of thermostate provided with the instrument. The temperature below room temperature was achieved by using a cooling system of Grant Instruments Co England.

Solution of specified concentration was taken in the sensor system. The instrument was calibrated for minimum and maximum values at desired temperature. For various values of "n" (representing the rps of the rotor), the resulting torque "S" was noted from the read out system. In this way readings were taken for all the solutions in the specified temperature range.

From the data obtained shear rate " $\dot{\gamma}$ ", shear stress " $\tau$ " and shear viscosity " $\eta$ " of the solutions were calculated by using following equations [6].

$$\dot{\gamma} = M \times n \quad (1)$$

$$\eta = (G \times S)/n \quad (2)$$

$$\tau = A \times S \quad (3)$$

where M, G and A are constants for the sensor system used with M = 5.41, A = 1.78, and G = 3.29.

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