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Measurement of the Mark-Houwink constant of ultra high molecular mass poly(methylmethacrylate) in toluene

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The aim of this work was to measure the Mark-Houwink constants and the c - η_{sp} - M_w relationship of ultra-high molecular mass poly(methylmethacrylate) in toluene solutions.

A set of ultra-high molecular mass (up to 2×10^7 g/mol) poly(methylmethacrylate), obtained in a previous work by B. Simionescu, was used together with a commercial set of lower molecular mass samples in order to cover two decades of molecular mass range. The intrinsic viscosity of the solutions were measured, to fit the Mark-Houwink and the c - η_{sp} - M_w relationships. The results are in agreement with the published literature but over a larger range of molecular mass with respect to the known literature. All the measurements were performed at 298 °K.

This work concerns in the rheological behavior of a polymer in solution, and has great interest in polymer processing. To study the viscoelastic behavior of a polymer system at high shear rate and/or high molecular mass (M_w) is a very difficult task, owing to the strong elastic behavior of the melt.

To overcome the difficulties, studying the behavior of high M_w melt, one of the possibilities is to use the correspondence between molten polymer at low shear rate and ultrahigh molecular mass polymer in solutions at high shear rate. To reach this aim, study the polymer over a large range of M_w is required. This implies great technical difficulties and, consequently, the lack of experimental data in the high shear rate range and/or high M_w polymer solutions. This lack has stopped an extension of the rheological theory.

When high M_w polymers are studied, generally, some new features have been measured because high M_w polymers are able to have large chain extension and interactions between chains also at low concentrations and low shear rate.

For example Simionescu *et al.* [1, 2] have measured the first normal stress difference, N_1 , vs. shear rate for poly(methylmethacrylate) (PMMA) of M_w about 2×10^7 g/mol in toluene at 2 and 6 (wt%) concentrations. He reported the presence of a three slope curve in the plot. To justify this behavior, Cates, McLeisch and Marrucci [3] suggested to introduce a transverse dimension of polymer chain in the tube model, to overcome the unrealistic continuous decrease of shear stress with shear rate found in the Doi-Edwards model for entangled polymers. From this idea it follows that three regions will occur in the plot of first normal stress difference vs. shear rate.

Almost all the literature concerns PMMA of M_w less than 2×10^6 g/mol [4, 5]. In 1955 Chinai *et al.* [4, 6] fitted the η - M_w relationships in a M_w range between 0.4×10^6 g/mol and 3×10^6 g/mol using toluene and other solvents. The η - M_w relationship, in toluene at very low M_w , was also investigated by Patroni [7] *et al.* (1965). In this paper the behavior of the system is theta solvent like owing to the low values of M_w (between 2×10^3 g/mol and 7×10^3 g/mol). In 1974 Graessley [8] investigated the flow properties of PMMA in diethyl-phthalate in a M_w range between 50×10^3 g/mol and 1.6×10^6 g/mol. He found results very similar to those for the more investigated polystyrene in the same conditions. In recent times [9, 10] the Mark-Houwink (M-H) constants for PMMA in tetrahydrofuran were investigated.

The M-H equation gives a qualitative measurement of the interactions between the polymer chain and the solvent. Generally, the exponent, a , of the equation was found to range from 0.5 (θ solvent) to 0.8 (good quality solvent). Therefore the quality of a solvent for a given polymer can be judged on its value of a . An higher value of a corresponds to an higher value of mean square end to end distance of the polymer chains. This has the meaning that the interactions between polymer and solvent are favored with respect of the interactions between segments to polymer chains.

In this work we have performed measurements of intrinsic viscosity, $[\eta]$, of PMMA in toluene, to obtain a fit of the Mark-Houwink relationship. After we have plotted the specific viscosity, η_{sp} , versus the overlapping coil parameters c $[\eta]$ and fitted the relative parameters of the equation [11]. In order to obtain a more accurate fit of the parameters we have used not only our own data but also data from the literature [4, 6–10, 12].

Two kinds of PMMA samples have been used: two commercial samples, supplied by Latek, (Eppelheim, Germany) for the two lower M_w samples, and two high M_w PMMA samples obtained by Simionescu using plasma-induced polymerization in a previous work [13]. Therefore, in the present study, four PMMA samples were selected to cover a range of two decades M_w . The molecular characteristics of the material used are shown in Table I. More information about the non-commercial high M_w PMMA can be found in ref. [13].

The solvent used was toluene.

The solutions were prepared and stored in dark bottles kept under gently shaking and rotation for one week

TABLE I Molecular mass (M_w), molecular mass distribution (M_w/M_n) of the used polymers and solvent

No.	Polymer	$M_w(10^{-6} \text{ g/mol})$	(M_w/M_n)	Solvent
1	PMMA	0.14*	1.13	Toluene
2	PMMA	1.56*	1.13	Toluene
3	PMMA	10.5**	1.3	Toluene
4	PMMA	19.2**	1.3	Toluene

* = Commercial sample as supplied by the Latek company.

** = Measured by B. C. Simionescu by light scattering in different solvent (ref. 15).

to be sure of a complete and homogeneous dissolution of the PMMA in the solvent.

The intrinsic viscosity, $[\eta]$, was measured by a Ubbelohde capillary viscometer (radius = 4×10^{-4} m) according to ASTM D2515. Flow times of between 90 s and 200 s were obtained, so kinetic energy correction can be neglected. The concentrations were chosen so that the range of relative viscosity fell between 1.1 and 1.8. The concentrations used were between 50 and 10^5 g/m³.

At least five different concentrations were used, for each sample, to calculate the limit:

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (1)$$

where

$$\eta_{sp} \equiv \frac{\eta_{solution}}{\eta_{solvent}} - 1 \quad (2)$$

and c is the concentration. The apparatus was held at 298 K.

Higher η_{sp} measurements were carried out by a rotary rheometer Physica (UDS200 model); the geometry used was a cone-plate geometry (radius = 3.75×10^{-2} m, angle = 1.74×10^{-2} rad, gap = 50×10^{-6} m). The measurements were performed in strain control mode and held at 298 K.

The values of $[\eta]$ versus M_w are shown in Fig. 1. Some of these data are taken from the literature [4, 12]

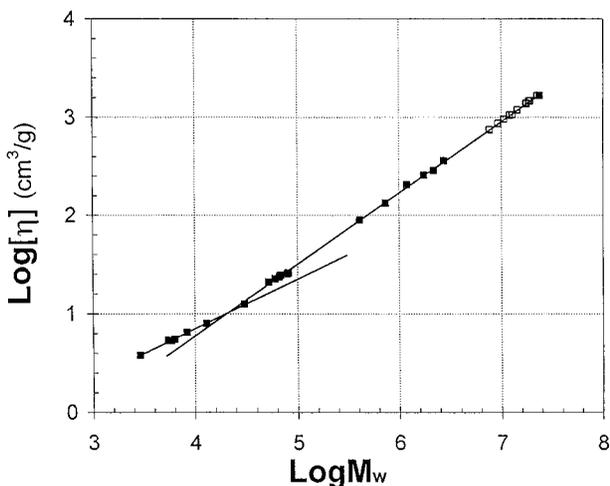


Figure 1 The intrinsic viscosity ($[\eta]$) as function of molecular mass (M_w) for PMMA in toluene. Hollow symbols are own data; filled symbols are literature data.

(filled symbols in Fig. 1) and they are well overlapped to our data (open symbols). According to the literature two regions can be distinguished in this plot: up to a critical molar mass, $[\eta]$ is proportional to $M_w^{0.5}$ following the equation:

$$[\eta] = K M_w^{0.5} \quad (3)$$

The best fit gives the values:

$$[\eta] = K M_w^{0.502 \pm 0.020} \quad (4)$$

and $K = 69.4 \pm 2$ (mm³/g). The critical molar mass, M_c , was found to lie between 30 000 and 40 000 (g/mol) according to ref. [8]. Beyond this critical value M_c the behavior of the polymer macromolecules is changing from a θ like state to a state where the effects of the excluded volume may not be negligible and follows the Mark-Houwink formula:

$$[\eta] = K M_w^a \quad (5)$$

where the Mark-Houwink exponent was found to be $a = 0.734 \pm 0.004$, and the constant $K = 66 \pm 3$ (mm³/g) in agreement with the literature [14].

The literature values are $a = 0.73$ and $K = 7.1$ (mm³/g), for PMMA in toluene at 298 K, but these data were measured on a M_w range between 0.4×10^6 and 3.3×10^6 g/mol.

The concentration dependence of the specific viscosity, η_{sp} , of dilute polymer solutions can be expressed as a power series in concentration, c :

$$\eta_{solution} = \eta_{solvent} \left(1 + \sum_{i=1}^k a_i c^i \right) \quad (6)$$

It has been proposed [11, 15] that this equation could be simplified by the following equation:

$$\eta_{sp} = c[\eta] + k_h(c[\eta])^2 + b_n(c[\eta])^n \quad (7)$$

According to Kulicke [11] in Fig. 2 we have plotted the specific viscosity, η_{sp} , versus the coil overlap parameter $c \cdot [\eta]$ for PMMA in toluene. In this plot the three

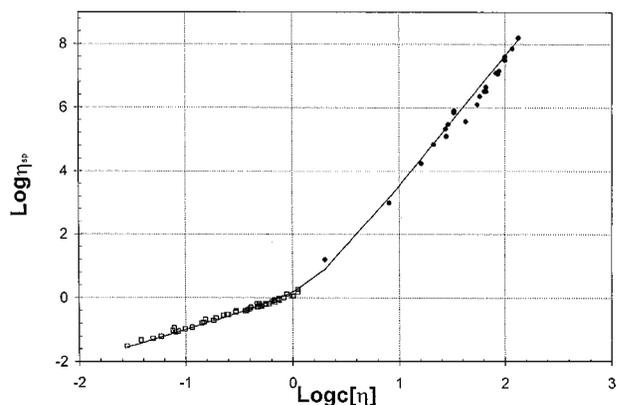


Figure 2 The specific viscosity (η_{sp}) as function of the overlapping parameter ($c \cdot [\eta]$) for PMMA in toluene. Square hollow symbols are data measured by Ubbelohde viscometer; circles filled symbols are data measured by Physica rotary rheometer.

regions (linear, quadratic, and proportional to $(c[\eta])^n$), according to Equation 7, can be recognized [16].

The set of the best fit parameter for Equation 7 is:

$$k_h = 0.32 \pm 0.02$$

$$b_n = 0.25 \pm 0.02$$

$$n = 4.06 \pm 0.24$$

It should be noted that the values of n do not agree with that theoretically [3] obtained from the relationship $n = 3.4/a = 4.59$ where a is the Mark-Houwink exponent and the value 3.4 is derived from the diffusion theory. Anyway the large range of the specific viscosity values renders the fit very difficult. These difficulties are reflected in the errors of the fit parameters.

The main features of this work are in the ultra high molecular mass of the polymer that has been used to confirm, experimentally, the validity of the Mark-Houwink equation in a molecular mass range where the dynamics of the polymer in solution are not well known. To this aim a set of poly(methylmethacrylate) samples whose molecular mass spans over two decades (from 0.01×10^7 g/mol up to 19.2×10^7 g/mol) have been used. Many data from the literature have been used in the low molecular mass range, where they are available, to reduce the errors in the fit of the parameters. Finally the concentration dependence of the specific viscosity has been fitted as a power series in concentration using a master curve.

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References

1. M. BERCEA, C. PEITI, B. SIMIONESCU and P. NAVARD, *Macromolecules* **26** (1993) 7095.
2. C. I. SIMIONESCU, S. IOSAN and B. C. SIMIONESCU, *Macromol. Chem. Macromol. Symp.* **20/21** (1988) 235.
3. M. E. CATES, T. C. B. MCLEISH and G. MARRUCCI, *J. Europhys. L.* **21** (1993) 451.
4. S. N. CHINAI, J. D. MATLACK, A. L. RESNICK and R. J. SAMUELS, *J. Polym. Sci.* **17** (1955) 391.
5. E. C. GINSBERG, T. G. FOX and H. F. MASON, *ibid.* **97** (1962).
6. S. N. CHINAI and R. J. SAMUELS, *ibid.* **19** (1956) 463.
7. E. PATRONI and U. BIANCHI, *Mackromol. Chemie* **52** (1966).
8. W. W. GRAESSLEY and H. W. PENSHERE, *J. Polym. Sci. Polym. Phys.* **12** (1974) 2347.
9. Y. CHEN, J. LI, N. HADJICHRISTIDIS and J. MAYS, *Polym. Bull.* **30** (1993) 575.
10. C. JACKSON, Y. CHEN and J. W. MAYS, *J. Appl. Polym. Sci.* **59** (1996) 179.
11. W. M. KULICKE, R. KNIEWSKE, R. J. MULLER, M. PRESCHER and H. KEHLER, *Angew. Makromol. Chemie* **142** (1986) 29.
12. Y. SHIMURA, *Bull. Chem. Soc. Of Japan* **40** (1967) 273.
13. B. C. SIMIONESCU, *J. Macromol. Sci. Chem.* **A22** (1985) 765.
14. BRANDUP, IMMERGUT (Eds.), *Polymer Handbook*, 3rd ed. 1990.
15. W. M. KULICKE, M. BOUDING and H. KEHLER, *Coll. & Polym. Sci.* **266** (1988) 793.
16. W. M. KULICKE and R. S. PORTER, *J. Polym. Sci. Polym. Phys. Ed.* **19** (1981) 1173.
17. T. G. FOX, *Polymer* **1** (1962) 111.
18. W. R. MOORE and R. J. FORT, *Mackromol. Chem.* **97** (1962) 929.