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Determination of the Molecular Weight of Polymers Using Scaling Phenomena in Critical Systems

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SUMMARY

In this article a method is proposed, for the determination of the molecular weight of polymers, based on the displacement of the critical solution temperature of two non-miscible liquids in presence of a polymer. This displacement obeys to a scaling law, i.e. a linear relation exists between the logarithm of the displacement and the logarithm of the molecular weight of the polymer or of the hydrodynamic volume of the polymer, $[\eta]M$.

INTRODUCTION

The study of the coexistence curve of two non-miscible liquids in the presence of a polymer has attracted some interest during the last years(1-5). It has been demonstrated that the critical solution temperature, T_c, of a binary liquid mixture is displaced to higher temperatures in presence of a small quantity of a polymer.

In a recent article(5) we have demonstrated that this displacement of T_c of the two non-miscible liquids in the presence of the polymer is due to a "polymeric" phenomenon and that it is directly related to the molecular weight of the polymer. In this article we will try to relate this phenomenon with the recent concepts of the scaling theory(6) in order to propose a simple method for the determination of the molecular weight of a polymer.

EXPERIMENTAL

The samples of linear polystyrene (PS) used in this work are anionically prepared and their polydispersity is very low ($M_w/M_n < 1,2$). The N, N-dimethylformamide (DMF) was lab grade (Merck), the cyclohexane (CH) and the methanol (MeOH) used were of reagent grade (Merck). If the DMF was in contact for a relatively long time with the air, it was distilled.

The turbidimetric measurements were conducted in hermetically closed tubes. The temperature at which homogeneity appeared was obtained by very slow heating of the tubes being under continuous stirring by hand in a water-bath. The rate of heating was lower than 0,1 °C per minute. The critical solution temperature (T_c) was visually determined within a precision of 0,1°C.

RESULTS AND DISCUSSION

In Fig.1 we give the variation of $\log\varepsilon'$ as a function of logM for the ternary system CH/DMF/PS in two different solvent compositions, 85 Vol % CH, Fig.1(a) and 75 Vol % CH, Fig.1(b), where ε' is equal to $(T_c-T_o)/T_o$ and T_o is the critical solution temperature of the binary system in presence of monomer styrene and T_c in presence of polystyrene, PS. M is the molecular weight of each PS sample. The concentration of the different samples of PS is always the same and equal to 5×10^{-3} gr/cm³.

In Fig.2 we give the variation of $\log\varepsilon'$ as a function of logM, for an-

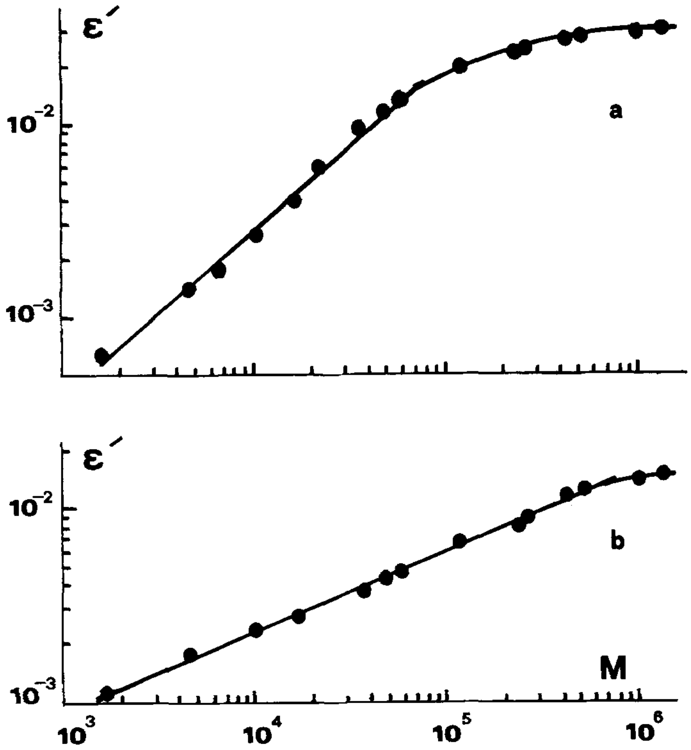

Fig.1. Variation of the reduced temperature, $\varepsilon' = (T_C - T_O)/T_O$, versus the molecular weight, M, for the system CH/DMF/PS.
(PS, $c = 0,5\times10^{-2}$ g/ml).
(a) : 85 Vol % CH,
(b) : 75 Vol % CH.

other ternary system, 72 Vol % CH/28 Vol % MeOH/PS 0,2%.

As we can see in Figs 1 and 2 we have a linear relation between logε' and logM for a large region of molecular weights of the polymer and it is easy to propose the relation

$$\varepsilon' = k\, M^{\nu'} \qquad (1)$$

in which k and ν' are constants characterizing the ternary system. More precisely for each system we have :

$$\varepsilon' = 5,75\times10^{-5} M^{0,40} \text{ (75 Vol \% CH/25 Vol \% DMF/0,5 \% PS)} \qquad (2)$$

$$\varepsilon' = 7,2\times10^{-7} M^{0,90} \text{ (85 Vol \% CH/15 Vol \% DMF/0,5 \% PS)} \qquad (3)$$

$$\varepsilon' = 5,0\times10^{-5} M^{0,47} \text{ (72 Vol \% CH/28 Vol \% MeOH/0,2 \% PS)} \qquad (4)$$

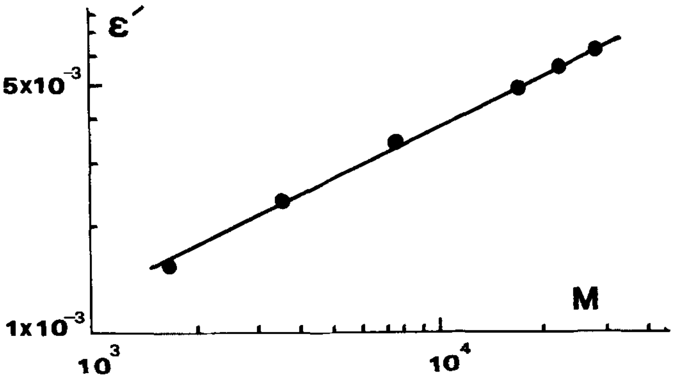

Fig.2. Variation of ε' vs. M for the system 72 Vol % CH/28 Vol % MeOH/PS
(PS, $c = 0,2\times10^{-2}$ g/ml).

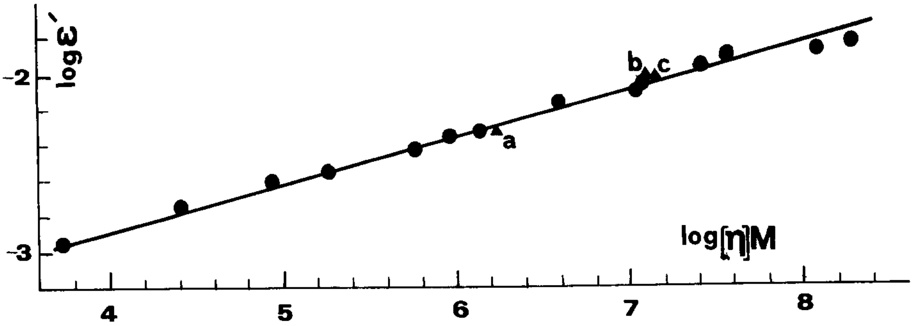

Fig.3. Variation of logε' vs. log[η]M for the system 75 Vol % CH/25 Vol % DMF/PS (PS, c=0,5x10^{-2}g/ml) (●), linear PS samples, (▲), star PS samples, (a : M=125.000, branch 15.600, b : M=312.000, branch 77.000, c : M=470.000, branch 50.000).

These relations give the scaling of the reduced temperature, ε', of the ternary system with the molecular weight of the polymer. The validity of the above relations (linearity between logε' and logM) is extended to M≃600.000 (Fig.1(b)), 50.000 (Fig.1(a)) and 30.000 (Fig.2) correspodingly.

It is well known that all the equations describing scaling phenomena are not valid for the entire range of molecular weights. The slope of the equation Mark-Houwink-Sakurada, for instance, changes in good solvents from 0,5 for the lower molecular weights to a value close to 0,8 for the higher molecular weights(7). A similar behaviour is observed in the relation between logε' and logM, especially in the case of the system 85 Vol%CH/15 Vol % DMF/0,5% PS (Fig.1(a)). Nevertheless a good linearity between logε' and logM is observed for our systems and this permits us to propose this relation as a new method for the determination of the molecular weight of a polymer sample using turbidimetric measurements.

It is evident that many methods exist for the determination of the molecular weight of a polymer (viscosity, osmometry, light scattering, G.P.C.) but we believe that the proposed here method is characterized by a high simplicity : having only a hermetically closed tube and two non-miscible solvents we can establish one calibration curve with three or four samples of a polymer of known molecular weight and we can use this curve for the determination of the molecular weight of other samples of this polymer.

Our results in Figs 1 and 2 are obtained with linear PS samples. The points obtained with star-shaped PS samples do not fit on the curves (5). Nevertheless using the product [η]M (an expression for the hydrodynamic volume(8)) instead of M we obtain a unique curve for all the PS samples (linear and star) as we can see in Fig.3. The plot logε'-log {[η]M} can be proposed as a "universal" method for the determination of the molecular weight of any polymer sample presenting different structures (linear, star, branched).

We would like to emphasize that our experimental results give a good accuracy in the determination of the molecular weight of a polymer sample using the curve logε'-logM.

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