

DETERMINATION OF THE MOLECULAR WEIGHT OF POLYSTYRENE FROM VISCOSITY MEASUREMENTS CARRIED OUT IN THE SOLVENT MIXTURES

M. TALU

Department of Chemistry, Faculty of Arts and Science, Gazi University, Teknik Okullar, 06500 Ankara, TURKEY

SUMMARY

The molecular weight of polystyrene was determined from viscosity measurements carried out in solvent mixtures. Toluene - chloroform mixtures of various percentages were used as solvent.

INTRODUCTION

It is known that Mark - Houwink relation

$$\{\eta\} = K' M^{\alpha'} \quad (1)$$

is used to calculate the molecular weights of linear polymers viscometrically. It is known that (η) is the limiting viscosity number and K' and α' are constants for a given polymer - solvent system and temperature at which the limiting viscosity number is determined.

In this work it was aimed to apply the Mark - Houwink relation, which is so far used for only single solvent systems, to the solvent mixtures system to calculate the molecular weight of some linear polymers.

For this purpose, the following equations were proposed to determine the values K' and α' which are required to calculate molecular weight from viscosity measurements in solvent mixtures.

$$K' = K_1 + (K_2 - K_1) (1 - f_1)^2 \quad (2)$$

$$\alpha' = \alpha_1 f_1 + \alpha_2 (1 - f_1) \quad (3)$$

where f_1 stands for the volume fraction of one solvent in the solution. K_1 , α_1 and K_2 , α_2 are constants for a given polymer - solvent system and temperature.

The values of K_1 , α_1 , and K_2 , α_2 are given in the references (Brandrup / Immergut, 1975) (Endo, Takeda, 1962) for polystyrene - toluene and polystyrene - chloroform systems.

EXPERIMENTAL

Polystyrene was supplied from PETKİM.

The polymer was fractionated by precipitation with methanol from toluene solution. The viscosity average molecular weight of the two fractions used were 322×10^3 and 199×10^3 respectively.

The viscosity measurements were carried out at $30 \pm 0.5^\circ\text{C}$ with Ubbelohde viscometer for the different volume percentages of toluene - chloroform mixtures. The calculated values of K' and α' the viscosity results are given in Table I. By using the values of K' and α' , the viscosity molecular weights of the polymers found from equation (1) are also given in Table I.

Table I. Viscosity Average Molecular Weights of Polystyrene Measured in the Toluene - Chloroform Mixtures.

Fraction I				
Toluene % V/V	$(\alpha) \text{ dl g}^{-1}$	α'	$K' \times 10^3 \text{ dl g}^{-1}$	$\bar{M}_v \times 10^{-3}$
100	0.85	0.720	9.29(Endo, Takeda, 1962)	322
90	0.95	0.727	9.15	335
80	1.05	0.735	9.03	340
70	1.10	0.742	8.81	332
60	1.20	0.750	8.51	341
50	1.35	0.757	8.13	369
40	1.31	0.764	7.65	343
30	1.27	0.772	7.09	323
20	1.26	0.779	6.45	322
10	1.24	0.787	5.72	323
00	1.16	0.794	4.90(Brandrup / Immergut, 1975)	323
Fraction II				
100	0.60	0.720	92.0(Endo, Takeda, 1962)	199
90	0.63	0.727	9.15	190
80	0.69	0.735	9.03	192
70	0.77	0.742	8.81	205
60	0.85	0.750	8.51	215
50	0.91	0.764	7.65	215
40	0.90	0.757	8.13	220
30	0.90	0.772	7.09	207
20	0.86	0.779	6.45	197
10	0.84	0.787	5.72	197
00	0.79	0.794	4.90(Brandrup / Immergut, 1975)	199

RESULTS AND DISCUSSION

The values of the molecular weights obtained in the solvent mixtures were given in Table I. The equations (2) and (3) were used to calculate K' and α' constants in the solvent mixtures used, the validity of which were proved in a previous study (Pulat, 1974).

As can be seen from Table I the values of the molecular weights obtained in the solvent mixtures are in agreement with those obtained in pure solvents.

Two points from these results deserve comment: Firstly, the highest value of (η) corresponds to that mixture ranging between % 20 and % 50. Therefore, the best solvent of polystyrene is the toluene-chloroform mixture containing 50 - 20 % of toluene (Margerison, 1967).

Secondly, viscosity average molecular weights of linear polymers can also be measured by using solvent mixtures instead of one solvent. So we suggest the equations (2) and (3) can be used for the calculation of K' and α' constants in Mark - Houwink equation, This application may be extended to copolymers.

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ÖZET

Bu çalışmada iki fraksiyona ayrılan polistiren örneklerinin farklı yüzdelerde toluen - kloroform karışımında intrinsik viskoziteleri tayin edilmiş ve bu intrinsik viskozite değerleri kullanılarak, aynı polistiren örneği için

$$(\eta) = K' M^{\alpha'} \quad (1)$$

eşitliğinden viskozite ortalama molekül ağırlıkları hesaplanmıştır. Yukarıdaki eşitlikte yer alan K' ve α' sabitlerine ait değerler

$$K' = K_1 + (K_2 - K_1) (1 - f_1)^2 \quad (2)$$

$$\alpha' = \alpha_1 f_1 + \alpha_2 (1 - f_1) \quad (3)$$

bağıntılarını kullanarak bulunmuştur. Bu bağıntılarda f_1 , çözeltide çözücülerden birinin hacim kesrini göstermektedir. K_1, α_1 ve K_2, α_2 ise polistiren - toluen ve polistiren - kloroform sistemleri için literatürde (Brandrup, Immergut, 1975) (Endo, Takeda, 1962) verilen sabitlerdir.

Her karışım için denel olarak tayin edilen vizkozite değerleri (2) ve (3) bağıntılarında bulunan K' ve α' sabitleri kullanarak, (1) eşitliğinden vizkozite ortalama molekül ağırlığı değerleri hesaplanmıştır. Aynı polistiren örneğine ait olan vizkozite ortalama molekül ağırlığı değerlerinin birbirlerine oldukça yakın çıktıkları görülmüştür.

Bundan başka bu polimer için toluen ve kloroform karışımının saf toluen ve kloroformdan daha iyi çözücü olduğu, özellikle % 20-50 toluen bulunduran karışımın çözücü olarak en etkili olduğu da anlaşılmaktadır (Margerison, 1967).

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