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The Mark-Houwink Constants for Poly(Methyl Methacrylate) in N,N-Dimethylformamide

I. Kössler[1], M. Netopilík[1], G. Schulz[2] and R. Gnauck[2]

[1] Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

[2] Zentralinstitut für Organische Chemie, AdW der DDR, Berlin-Adlershof, German Democratic Republic

Summary

The Mark-Houwink constants $K = 2.5 \times 10^{-2}$, $a = 0.625$ were determined for the system poly(methyl methacrylate) - dimethylformamide at 25°C using narrow fractions (M_w/M_n from 1.00 to 1.55) in the molecular weight range from 1.19×10^5 to 1.94×10^5 as determined by the light scattering method and osmometrically.

In order to evaluate GPC records of poly(methyl methacrylate)(PMMA) in dimethylformamide (DMF), it was necessary to determine the Mark-Houwink constants for PMMA in DMF at 25°C.

The measurements were performed using fractions of PMMA obtained by radical polymerization. Fractions with a narrow molecular mass distribution were prepared by Poláček (POLÁČEK et al. 1976) by using the precipitation chromatographic method. They were characterized by the mass and number average molecular masses (M_w,M_n). The M_w values were determined by the light scattering data were extrapolated to zero concentration and zero angle of measurement by employing a standard procedure. The M_n values were determined in toluene at 50°C with a Knauer membrane osmometer.

The viscosities were measured with an Ubbelohde viscometer at 25°C in DMF. With respect to the hydroscopicity of the solvent, both the preparation of solutions and viscosity measurement took place under nitrogen which was dried by passing through a column packed with silica gel. The concentration of solutions was in the range 1×10^{-4} - 11×10^{-4} g/cm^3. The intrinsic viscosity was determined in a standard way. The , M_w and M_n values are given in Table 1; the M_w and M_n values calculated from GPC records are given for the sake of comparison. The accordance is satisfactory.

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Table 1: M_w and M_n values obtained from the light scattering, osmometric, GPC and viscosity measurements

No	M_w x10^{-5}	M_n x10^{-5}	M_w/M_n	M_w x10^{-5} GPC	M_n x10^{-5} GPC	M_w/M_n GPC	cm^3/g
1	0.826	0.825	1.00	0.93	0.78	1.19	29.7
2	1.24	1.21	1.03	1.32	1.10	1.20	39
3	1.73	1.54	1.12	1.80	1.36	1.32	45
4	2.02	1.74	1.16	2.35	1.63	1.44	51.7
5	2.87	2.33	1.23	2.81	2.17	1.29	61
6	3.60	2.57	1.40	3.51	2.40	1.46	77
7	5.27	3.13	1.68	5.43	2.80	1.94	95.5
8	11.0	7.09	1.55	12.7	6.53	1.94	162

The following values were found for the parameters of the Mark-Houwink equation at 25°C: $K = 2.5 \times 10^{-2}$, $a = 0.625$; for determination of these parameters, M_w values were used. By using M_n values, $K = 4.04 \cdot 10^{-3}$, $a = 0.787$. Using data in a paper published earlier (KAMBE 1968), the following values were calculated for 10°, 30°, and 50° resp.: $Kx10^2 = 2.94$, 2.07, and 2.07; $a = 0.594$, 0.628, and 0.632. Our values adequately fit in with the temperature dependences of both parameters which can be constructed using these data.

References

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