

NOTES

*Osmotic and Viscometric Characterization of Poly(*p*-chlorostyrene) and Poly(*p*-methoxystyrene)*

Viscosity-molecular weight relationships for fractionated samples of poly(*p*-chlorostyrene)¹ and poly(*p*-methoxystyrene)² have been reported previously. In the present study, number-average molar masses \bar{M}_n and limiting viscosity numbers $[\eta]$ have been determined for several unfractionated low-conversion polymers of *p*-chlorostyrene and *p*-methoxystyrene. Monomers were prepared as described previously³ and bulk polymerized to about 10% conversion by a free-radical mechanism using 1,1'-azoisobutyronitrile as the initiator. The reactions were carried out in sealed evacuated tubes at 60° and 80°C, polymers were precipitated by slow addition to a tenfold excess of methanol, collected in sintered-glass crucibles, and dried to constant weight in a vacuum oven at 50°C.

Determination of \bar{M}_n

Osmotic pressures π were measured on toluene solutions of polymers by a static equilibrium procedure at 25°C. The osmometers⁴ were similar to those of Breitenbach and Forster⁵ but with a larger cell volume of about 2.5 cm³. They had a total membrane area of approximately 8 cm² and were designed for filling and emptying through the 1-mm measuring capillary with a syringe and long cannula. Cellulose acetate membranes prepared by Vaughan's method⁶ were used.

At least four separate polymer solutions with concentrations between 0.25% and 1% (w/w) were used for each polymer sample. The osmometers were charged with solution above the equilibrium osmotic height, and the difference in head between solution and solvent capillaries was measured periodically. The process was then repeated with the osmometers charged with

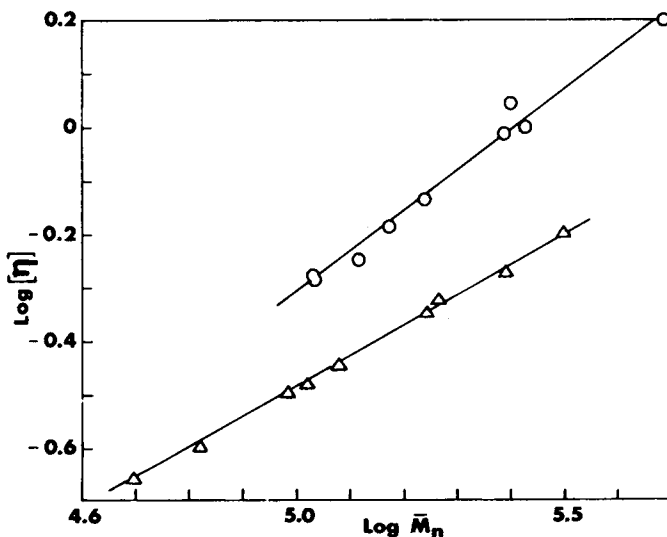


Fig. 1. Plots of $\log [\eta]$ vs. $\log \bar{M}_n$: (O) poly(*p*-methoxystyrene); (Δ) poly(*p*-chlorostyrene).

TABLE I
 Polymerization and Characterization of Poly(*p*-chlorostyrene)
 and Poly(*p*-methoxystyrene)

Polymer	Polymerization		$[\eta]$, dl/g	$\bar{M}_n \times 10^{-5}$	$A_2 \times 10^4$, (cm ³ mole)/g ²
	Temp., °C	Con- version, %			
<i>p</i> -Cl- styrene	60	13.5	0.220	0.49	1.96
	60	13.3	0.255	0.66	1.82
	80	13.1	0.320	0.96	1.71
	80	15.8	0.331	1.04	1.68
	60	6.7	0.360	1.19	1.54
	80	8.2	0.450	1.76	1.44
	60	10.8	0.475	1.83	1.39
	60	11.9	0.534	2.46	0.90
	80	14.2	0.631	3.16	0.66
	<i>p</i> -MeO- styrene	60	8.9	0.545	1.07
60		7.2	0.522	1.08	3.51
80		4.5	0.570	1.31	3.43
60		9.0	0.657	1.50	3.18
60		9.6	0.738	1.74	2.88
60		8.5	0.975	2.46	2.66
80		6.8	1.10	2.53	2.49
60		9.8	1.00	2.72	2.25
60		1.0	1.57	4.90	—

solution below the equilibrium osmotic height. Osmotic equilibrium curves of Δh versus time were plotted for each solution, and the osmotic height was extrapolated to zero time.⁷ Number-average molar masses \bar{M}_n were obtained by linear extrapolations of $(\pi/c)^{1/2}$ as functions of concentration c to zero concentration as described previously.⁸ Osmotic second virial coefficients A_2 were also calculated and showed the expected decrease with increase of molecular weight.

Determination of $[\eta]$

Limiting viscosity numbers $[\eta]$ were measured in toluene solutions at 25°C using Ubbelohde dilution viscometers. Reduced specific viscosities η_{sp}/c were plotted as a function of concentration c (g/100 cm³) and extrapolated to zero concentration to yield $[\eta]$. The kinetic energy correction was not applied. The Huggins constants k' obtained from the slopes of the plots were independent of molecular weight and were 0.60 for poly(*p*-chlorostyrene) and 0.38 for poly(*p*-methoxystyrene).

RESULTS

Data relating to the polymers are recorded in Table I. Plots of $\log [\eta]$ versus $\log \bar{M}_n$ (Fig. 1) give straight lines which were fitted by the method of least squares to give the relationships

$$[\eta] = 4.69 \times 10^{-4} \bar{M}_n^{0.57} \text{ (coefficient of correlation} = 0.999)$$

For poly(*p*-methoxystyrene)

$$[\eta] = 9.70 \times 10^{-5} \bar{M}_n^{0.74} \text{ (coefficient of correlation} = 0.991)$$

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