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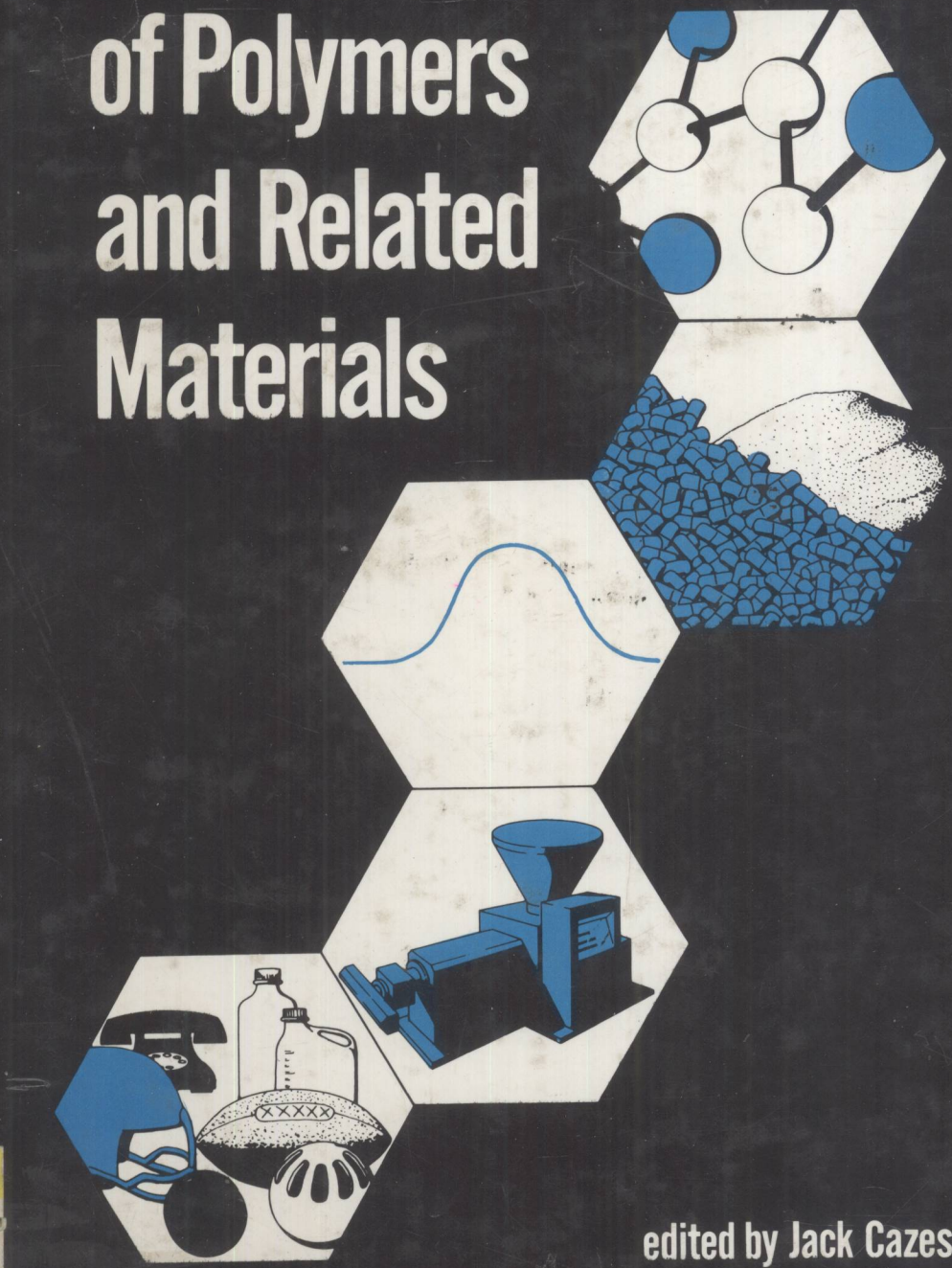
Liquid Chromatography of Polymers and Related Materials



edited by Jack Cazes

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Liquid Chromatography of Polymers and Related Materials

Edited by JACK CAZES

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PREFACE

Published in this volume are the proceedings of the International Symposium on Liquid Chromatographic Analysis of Polymers and Related Materials, which was held on October 13-15, 1976 at the Rice-Rittenhouse Hotel in Houston, Texas. Assembled here are thirteen papers covering a range of topics of interest to those involved in fractionation and characterization of macromolecular systems.

Jack Cazes
Editor

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CHARACTERIZATION OF P(MMA) AND P(MMA/MAA) BY LOW ANGLE LASER LIGHT SCATTERING PHOTOMETRY, GPC, AND VISCOMETRY

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ABSTRACT

Solution properties of poly(methyl methacrylate), P(MMA), and (methyl methacrylate/methacrylic acid) copolymers, P(MMA/MAA), were investigated using low angle laser light scattering (LALLS), gel permeation chromatography (GPC) and viscometry techniques. The molecular weight and compositional ranges studied were from 2.6×10^4 to 3×10^6 and from p(MMA) to a 50/50 P(MMA/MAA) copolymer ratio, respectively.

In tetrahydrofuran (THF) solvent, the exponent of the Mark-Houwink equation was found to vary between 0.73 for P(MMA) to 0.63 for 50/50 copolymer. A plot of the exponent of the Mark-Houwink equation versus the % acid in the copolymer appears to be linear and approaches a value of 0.50 as the % acid approaches 75%. A comparison between the weight average molecular weight ($\bar{M}w$) obtained by LALLS techniques and those obtained by GPC and viscometry using polystyrene calibration standards indicated the P(MMA) and P(MMA/MAA) elute from GPC according to their hydrodynamic size. This allows the estimation of the molecular weight distribution (MWD) from GPC chromatograms using the Universal Calibration method.

INTRODUCTION

With the possible exception of polystyrene and other olefinic polymers, poly(methyl methacrylate) P(MMA) is probably the most studied polymer, for its solution properties have been reported by a number of investigators (1-6). However, relatively little is known about its methacrylic acid copolymers, P(MMA/MAA).

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Panov and his co-workers, (7-10) have studied some of the solution properties of these copolymers in N,N-dimethyl formamide (DMF) and ethylene dichloride (EDC) at various molar ratios of the acid and ester comonomers. Panov and Frenkel (7) reported that (MMA/MAA) copolymers in EDC solvent do not follow the Mark-Houwink type relationship between the intrinsic viscosity, $[\eta]$, and molecular weight, M. Their results showed a highly non linear relationship between the log $[\eta]$ and log [M] for P(MMA/MAA) with $M \geq 10^5$ and MAA mole % $\geq$ 10%. Based on these results Panov and Frenkel (7) concluded that this non-linear $[\eta]$-M relationship might also hold true for other solvents. This conclusion implies that the (MMA/MAA) copolymers will not fractionate in the gel permeation chromatograph, GPC, according to their molecular hydrodynamic size, hence making the so called "Universal Calibration" method (11) of estimating the molecular weight distribution from the GPC chromatogram invalid. Thus, a primary purpose of this work was to ascertain the validity of Panov and Frenkel's conclusion for the P(MMA/MAA) in THF solvent. Our other objective was to determine qualitatively the existence of any dependence of the characteristic ratio $C_n = \frac{\langle r^2 \rangle_o}{n\ell^2}$ on the acid molar ratio in P(MMA/MAA).

EXPERIMENTAL

Synthesis

Most of the copolymers were prepared in THF (redistilled from $LiAlH_4$) and the remainder in toluene (redistilled from Na). For a typical synthesis, a heavy walled, 175 ml pressure bottle was oven dried at 170°C and cooled under dry N_2. The addition of reagents was carried out under a blanket of dry N_2 and subsequently the bottle sealed via a Teflon sleeve fitted over the bottle's stopper. To the reaction bottle were added 100 ml THF, 15 ml(14.1g, 0.14 mole) MMA, which had been passed through neutral $A\ell_2O_3$, 12 ml (12.2g, 0.14 mole) MAA, vacuum redistilled, and 0.1g of t-butyl hydroperoxide. The solution was heated to 70°C for 48 hrs. and the product recovered by pouring the viscous solution into excess n-hexane. The precipitate was washed several times with n-hexane and dried in a vacuum oven at 60°C for 18 hours. The acid content was found to be 48%. For copolymers with other acid contents, the monomer feeds were adjusted accordingly. For copolymers with M_w's less than 100K, bromotrichloromethane was used as the M_w regulator. To prepare the fully methylated samples, the copolymers were dissolved in $CHCl_3$-MeOH mixtures and treated with an excess of diazomethane in ether.

Compositional Analysis

The copolymers were analyzed either by titrating them with standard base or by using ^{13}C-NMR. To titrate the copolymers, samples were analytically weighed into a beaker and dissolved in an EtOH-H_2O mixture. The solution was titrated to a phenolphthalein endpoint with standardized 0.15 N aqueous KOH.

For ^{13}C-NMR analyses, 0.3g samples were dissolved or swelled in ca. 2g of a 50/50 mixture of pyridine and pyridine-d_5, both compounds being directly weight into a 10mm NMR tube. The ratios of ester to acid were determined by comparing the integrals of the carbonyl peaks from 175 to 185ppm relative to TMS.

M and [η] Measurement

All solutions in this study were prepared in THF (distilled in glass grade, Burdick and Johnson) stabilized with 0.1% Ionol. The weight average molecular weights (M_w) were measured using the recently developed low angle laser light scattering (LALLS) photometer (13-15).

The Rayleigh factors of the different samples were measured at an angle of 4° scattering over a range of concentrations. The M_w and the second virial coefficient A_2 were calculated by linear regression analysis from the intercept and the slope of KC/R_θ (K is the polymer constant and R_θ is the Rayleigh factor) versus concentration (C) respectively. The C versus the KC/R_θ plot for all samples had a linear regression correlation factor of better than 0.99 (1 is perfect linear correlation).

The solution viscosities were measured by an automatic viscounter (FICA VISCOMATIC) over a concentration range, and were adjusted for the different molecular weight samples such that the efflux times through the capillary were between 20 to 40 secs. The intrinsic viscosities were obtained from the intercepts of both the (ηsp/C) and ln (ηr)/C versus C plots. Both plots were linear within the concentration ranges of the measurements.

The GPC analyses were carried out in a modified and automated (data acquisition and reduction are computerized) Waters Associates Model 200. The modifications on the GPC were described elsewhere (14). Five 4 ft fractionating columns with permeability limits ranging from 10^3 Å to 5×10^6 Å (Water's Associates designation) and column efficiencies of from 800 to over 1500 plates/ft were used. The calibration standards used

were narrow molecular weight distribution (MWD) polystyrenes supplied by Pressure Chemical Co. and the National Bureau of Standards (NBS-705). No band broadening corrections were made in calculating the the value of M_w from the GPC data.

Results and Discussions

The $[\eta]$-M relationships for both P(MMA) and a 25 mole % MAA copolymer in Figure 1 show a good linear correlation. In fact, linear regression analyses of the $[\eta]$-M data exhibited correlation factors of 0.98 or higher for all samples. This linearity held throughout the molecular weights (2.6×10^4 to 3×10^6) and MAA content ranges (0 to 50%) studied. Thus it appears that Panov's and Frenkel's conclusion does not hold for P(MMA/MAA) in THF solvent.

A linear regression analysis of the log $[\eta]$-log M data gave the Mark-Houwink coefficients K and exponents α. The value of α was found to decrease with increasing acid content of the P(MMA/MAA). A plot of α and K versus the acid content of the copolymer is exhibited in Figure 2. The relationship between α and mole % MAA appears to be linear and extrapolation to zero acid content (PMMA) shows an α value of 0.75. Extrapolating the value of α to 0.50, indicates the theta condition at room temperature for P(MMA/MAA) in THF to be at 75 mole % MAA content. The second virial coefficient A_2, also appears to decrease with increasing acid content from 6.0×10^{-4} for P(MMA), to 3.4×10^{-4} for a 50 mole % P(MMA/MAA) with equivalent molecular weights.

A comparison of the M_w data obtained by the LALLS and GPC - "Universal Calibration" techniques shown in Table I, indicate good agreement. The M_w values for the linear portion of the GPC calibration (8×10^5 to 5×10^4) curve, agree with the light scattering values within 15%. These results indicate that (MMA/MAA) copolymers (up to 50 mole % MAA) in THF at room temperature fractionate in GPC according to their molecular hydrodynamic size in solution.

The characteristic ratios C_n were calculated from the K_θ in THF (a good solvent) using both the Fox-Flory (F-F) (16)

$$[\eta]^{2/3} M^{-1/3} = K_\theta^{2/3} + B_1 (M/[\eta]) \qquad (1)$$

and the Stockmayer-Fixman (S-F) (17)

$$[\eta]M^{-1/2} = K_\theta + B_2 M^{1/2} \qquad (2)$$

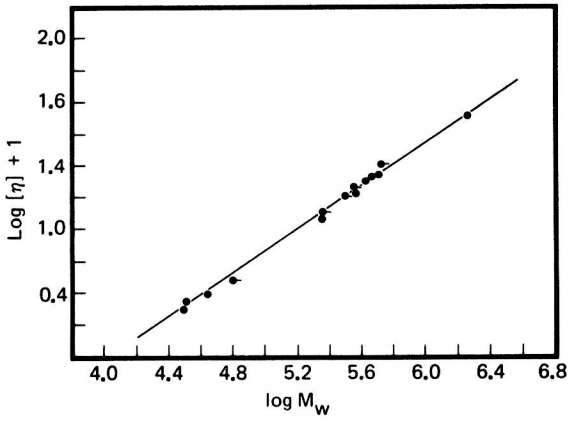

Figure 1. A logarithmic plot between [η] and M for both P(MMA) ●- and 25% MAA copolymer ● .

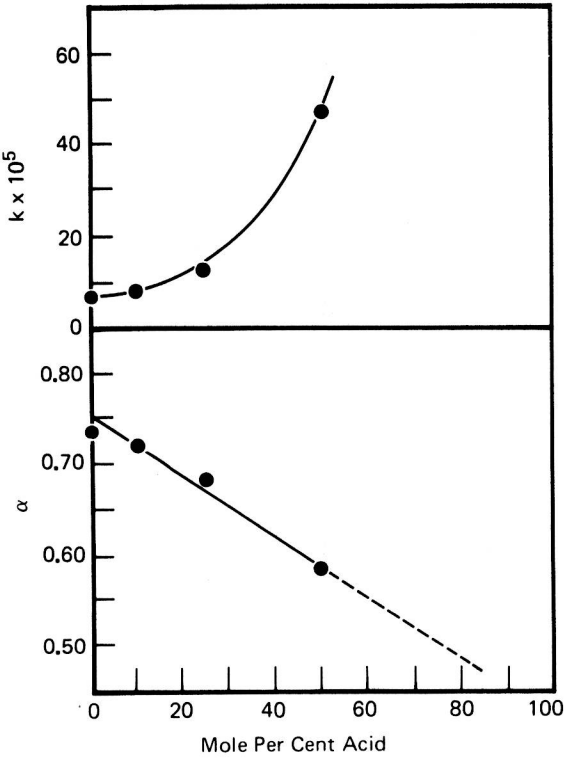

Figure 2. The Mark-Houwink exponent α and coefficient K plotted against percent MAA in the copolymer.

TABLE I

Comparison of the M_w Obtained by GPC-Universal Calibration and Light Scattering Techniques

Sample ID	Mole % MAA	M_w	
		GPC*$\times 10^{-3}$	LALLS$\times 10^{-3}$
88-2M	0	370	345
88-3M	0	510	513
103-2M	0	650	667
96-2M	0	765	830
108-2M	0	1100	1250
10-3	10	56	50
21-1	10	58	60
10-6	10	82	81
108-2	10	1230	1250
16-3	25	56	49
10-2	25	57	50
10-5	25	79	68
88-2	25	350	357
88-3	25	545	546
04-49	25	576	546
103-2	25	625	667
02-4	25	670	690
10-4	50	32	26
10-1	50	50	43
96-2	50	805	1042

*Average of Triplicate values.

extrapolation techniques. Figure 3 shows a plot of the $[\eta]M^{-1/2}$ versus $M^{1/2}$ for P(MMA) and a 25 mole % acid copolymer. A linear regression analysis of the $[\eta]$-M data following both equations (1) and (2) gave correlation factors of greater than 0.95 for all molecular weight and acid content ranges investigated. The root mean square end to end distances $\langle r^2 \rangle_o$ were computed from

$$\langle r^2 \rangle_o = [K_\theta/\Phi]^{2/3} M \qquad (3)$$

where Φ is the Flory constant.

The extrapolated values of K_θ and the calculated values of $\langle r^2 \rangle_o$ and C_n for the different molar contents of MAA are presented in Table II. The K_θ obtained by Chinai and Valles (2) for P(MMA) (the tacticity of which was not reported) in a theta solvent was 5.9×10^{-4}. This agrees reasonably well with the average value of 6.0×10^{-4} we obtained using the Fox-Flory

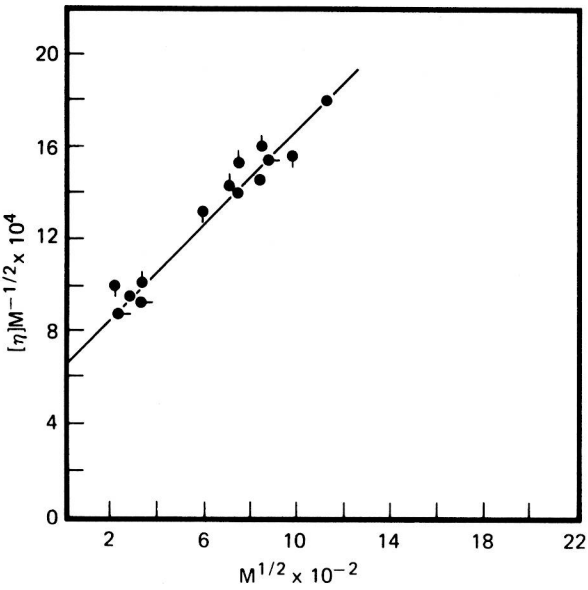

Figure 3. The Stockmayer-Fixman extrapolation technique for estimating K_θ. P(MMA) ● , 10% MAA ◗ , 25% MAA ◖, 50% MAA ◒ .

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