A Rapid Procedure for the Determination of Viscosity–Molecular Weight Relations

T. Kilp and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.
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ABSTRACT: A rapid procedure is described for the determination of viscosity–molecular weight relations for polymers. The method involves the preparation of a polymer of the desired composition containing small amounts of vinyl ketone units. This polymer is subjected to random scission by photodegradation in solution in the desired solvent. Single point measurements are made of the solution viscosity and osmotic pressure of aliquots removed at various stages in the degradation process. Since the molecular weight distribution will approach the most-probable or Flory distribution as the degradation progresses, after two or three breaks per chain the ratio of weight to number average will be very close to 2.0. The number average molecular weight is known from osmotic data and since the form of the distribution is known, a relation can be derived between solution viscosity and desired molecular weight average. Results on polystyrene-*co*-MVK in toluene are in good agreement with those obtained by classical procedures.

Viscometry is one of the most powerful yet simple tools available for the study of polymers. The wealth of information available from this source is paralleled by very few techniques. The ability of polymers to enhance the viscosity of a solvent, even in very dilute concentrations, is a function of the hydrodynamic volume of the macromolecule in the particular solvent. It has long been recognized that for a series of homologous polymers with similar molecular weight distributions, the intrinsic viscosity (limiting viscosity number) increases with increasing molecular weight.

The two quantities are related through the well-known Mark–Houwink equation

$$[\eta] = KM^a \tag{1}$$

where K and a are empirical constants determined for a polymer–solvent pair at a specified temperature. The attraction of this method of molecular weight determination lies in the simplicity and precision with which intrinsic viscosities can be measured. However, absolute molecular weights cannot be determined from measurements of solution viscosities alone. For each polymer–solvent pair at a specific temperature, the dependence of the intrinsic viscosity upon molecular weight must be established empirically by comparison with molecular weights determined by an absolute method. Thus values of the constants K and a are normally determined from a double logarithmic plot of intrinsic viscosity vs. molecular weight as determined on a number of fractions, for example, via osmometry or light scattering. The use of eq 1 then results in either a weight average or number average molecular weight, depending upon the absolute method used in deriving the empirical relationship.

Difficulties arise from the requirement that all samples used in establishing the relationship should, in principle, have identical or known molecular weight distributions. A variance in sample dispersities results in a failure to establish a consistent relationship between intrinsic viscosity and molecular weight.[1] Therefore, in order to obtain meaningful results, these disparities are minimized by careful fractionation and refractionation of the samples to be used. This usually requires a great deal of rather tedious labor to obtain and characterize the fractions.

We wish to describe an alternative procedure which is both faster and may indeed give a more reliable estimate of K and a.

It is now well established that a polymer undergoing a random scission process will rapidly approach a "normal" random distribution of molecular weights, regardless of the initial starting distribution.[2-5] For such a normal distribution, the ratio of weight average molecular weight $\overline{M}_w$ to the number average $\overline{M}_n$ will be equal to 2.0. By causing a polymer to undergo random scission, it is therefore possible in principle to produce a series of samples of differing molecular weight, but with the same known polydispersity. Measurements of the intrinsic viscosity and number average molecular weight by osmometry of a series of such samples should yield the desired relationship. The procedure was further simplified by using single point determinations of the intrinsic viscosity and the osmotic pressure.

One method of inducing a random scission process is to photodegrade a polymer containing small amounts of vinyl ketone groups in solution in a suitable solvent. If the number of ketone units is small (i.e., <2 wt %) they are unlikely to affect the hydrodynamic volume of the remainder of the polymer chain. Hence one should obtain results applicable to polymers of the major component alone. This is the basis for our procedure.

Experimental Section

A styrene–methyl vinyl ketone (1%) copolymer (PS-MVK-1) was prepared by bulk polymerization using 0.1 mol % benzoyl peroxide as initiator. The monomer mixture was degassed in a glass tube by four freeze–thaw cycles before being sealed off under vacuum. Polymerization was carried out for 18 h at 60 °C after which the seal was broken and the polymer precipitated in methanol. The polymer was reprecipitated twice more from a benzene solution into methanol, then dried under vacuum at 80 °C for 12 h. The ketone content was determined via a calculation using the reported[6] reactivity ratios of the two monomers. The polymerization was carried out to a total conversion of 23.5%. The initial polydispersity of the polymer as determined by gel permeation chromatography was 1.57 and its number average molecular weight was 197 000 by osmometry in toluene.

A second styrene–methyl vinyl ketone (2%) copolymer (PS-MVK-2) was prepared by emulsion polymerization. Its number average molecular weight by osmometry in toluene was 276 000 with a dispersity of 4.61 by GPC. The high initial polydispersity of 4.61 is typical of values received through emulsion polymerization techniques.

The polymers were dissolved in toluene at a concentration of 0.4 g dl^{-1}. Solutions were exposed in a quartz cell to the full spectral output of a 250 W medium pressure mercury arc lamp (Associated Electrical Industries, ME/D, box type).

Solution viscosities were measured using an Ubbelohde type viscometer which was part of an automatic apparatus previously described.[7] This enabled the determination of solution flowtimes to the nearest millisecond. However, this type of sensitivity is not a requisite for the application of our technique.

Intrinsic viscosities were determined through the application of the Solomon–Ciuta[8] equation:

$$\eta_{sp} - \ln \eta_r = [\eta]^2 c^2/2 \tag{2}$$

where η_{sp}, η_r, and $[\eta]$ are specific, relative, and intrinsic viscosities, respectively, and c is the concentration of the polymer solution in grams deciliter^{-1}. This involves only a single measurement of the solution and pure solvent efflux times at one concentration and pro-

Table I
Validity of Single Point Determination of Intrinsic Viscosity

Mol wt	Max dispersity	$[\eta]^a$	$[\eta]^b$	% deviation
411 000	1.06	1.261	1.260	0.08
160 000	1.06	0.645	0.640	0.15
51 000	1.06	0.282	0.284	0.70

[a] Value from single point determination. [b] Value from dilution series.

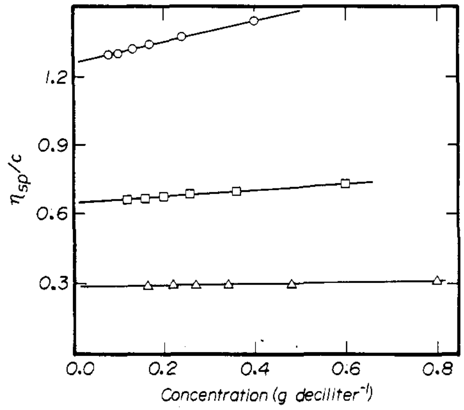


Figure 1: Determination of $[\eta]$ by dilution series. Molecular weights: (○) 411 000; (□) 160 000; (△) 51 000.

vides an extremely simple and rapid means of determination of the desired quantity.

For dilute solutions (less than 0.5% w/v) of polymers of molecular weight in the range of 10^4 to 10^5, the single point determination of $[\eta]$ generally yields results in good agreement with those determined by a dilution series with subsequent extrapolation to zero concentration. The results of a check on the validity of this expression are listed in Table I and shown in Figure 1 for a series of narrow molecular weight distribution polystyrene samples (GPC calibration standards, Pressure Chemical Co.).

The single point values were all determined for a polymer concentration of 0.400 g dl^{-1}. It can easily be seen that the agreement of the values derived by the two methods is excellent, the percent deviation increasing slightly with decreasing molecular weight. However, the error is less than 1% over the molecular weight viscosity measurements.

Molecular weight distributions were measured on a Waters Associates Model 200 gel permeation chromatograph using bioglass columns and *n*-butyl acetate solvent. Results were not corrected for possible line broadening or skewing.

Osmotic pressures were determined on a Hewlett-Packard Model 502 high speed membrane osmometer using type 08 S & S membranes and toluene as solvent.

The use of osmometry in the determination of polymer number average molecular weights commonly requires measurements at a series of concentrations and extrapolation to zero. Data are often analyzed with the use of the equation derived by Flory:[9]

$$\pi/c = (\pi/c)_0(1 + \Gamma_2 c + g\Gamma_2{}^2c^2) \tag{3}$$

where π is osmotic pressure, c is concentration in g dl^{-1}, $(\pi/c)_0 = RT/\overline{M}_n$ is the extrapolation back to zero concentration, Γ_2 is a parameter which varies as the polymer solvent interaction, and g is another parameter, often approximated by 0.25.

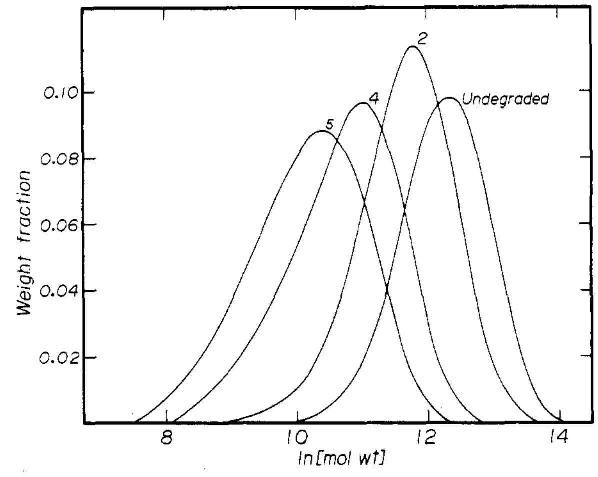


Figure 2: Molecular weight distribution of PS-MVK-1 as a function of the following irradiation times: (2) 75 min; (4) 184 min; (5) 1262 min.

From this it can be seen that if Γ_2 and c are sufficiently small, the power term can be neglected and the resulting plots of π/c vs. c for a series of homologous polymers in a common solvent should all have an identical slope. Once the value of the slope is established through a dilution series, subsequent molecular weights can be determined by linear extrapolation of single point osmotic pressures, hence evaluating the $(\pi/c)_0$ intercept algebraically.

Three samples of the irradiated polymers were successively diluted and their osmotic pressures measured in order to determine a value for their slope. Results are presented in Table II. Each sample has a different molecular weight, but similar molecular weight distribution. It can be seen that the slopes are fairly constant. A mean value of 0.0195 was therefore used in the subsequent determination of molecular weights.

Results and Discussion

The main experimental problem in the determination of the constants for the Mark–Houwink equation is the need for uniformity in the molecular weight distributions for the samples utilized. This does not imply that the samples must be monodisperse; polymers of a higher but constant known dispersity are equally suitable.

The photodegradation of various polymeric systems has been extensively studied in recent years. Two primary modes of decomposition have been well established: random degradation and chain unzipping. The former is characterized by random cleavage of the polymer chain resulting in fragments which are large in comparison to the monomer unit. Several authors (see above) have presented treatments of theory and calculations of molecular weight distributions for polymers undergoing random scission and cross-linking. Of prime importance to our studies is the result that polymers undergoing random degradation rapidly approach a most probable distribution which is characterized by the following relationship between the average molecular weights

$$\overline{M}_n:\overline{M}_v:\overline{M}_w = 1:[(1 + a)\Gamma(1 + a)]^{1/a}:2 \tag{4}$$

where $\Gamma(1 + a)$ is the γ function of $(1 + a)$. Therefore, after a certain number of initial chain breaks, all distributions are normal. Aliquots of the solution taken after various periods

Table II
Results Used in Converting Single Point Osmotic Pressures to Corresponding $\overline{M}_n$ Values

Polymer	Irradiation time, min	$(\pi/c)_0$	M_n	Slope of dilution series	Correlation coeff
PS-MVK-1	80.0	0.38	78 000	0.0200	0.998
PS-MVK-2	100.0	1.09	27 000	0.0206	0.982
PS-MVK-2	150.0	1.47	20 000	0.0178	0.954

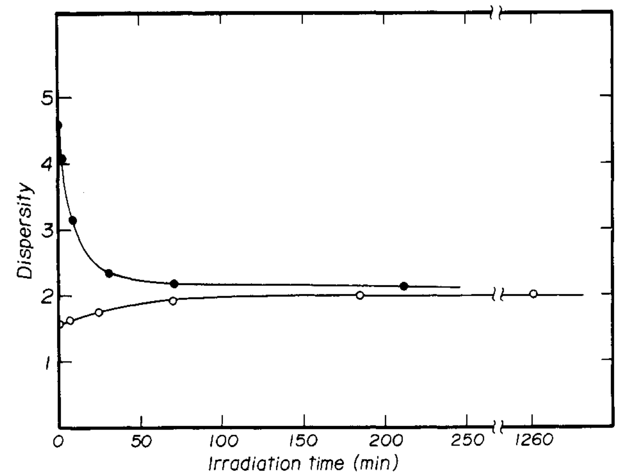
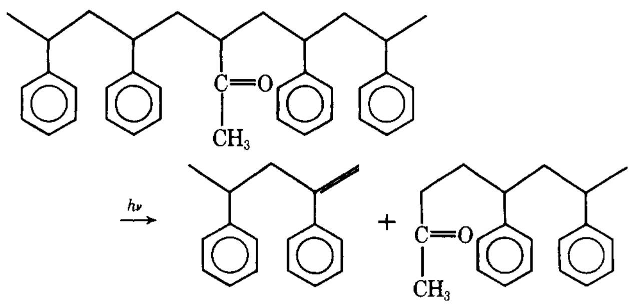


Figure 3. Dispersities of (○) PS-MVK-1 and (●) PS-MVK-2 as a function of irradiation time.

of irradiation should thus provide a series of homologous polymers with identical breadth of distribution.

The polymers chosen for initial studies were polystyrenes containing a small amount of methyl vinyl ketone. Chain scission is caused by the classic Norrish type II reaction.



The degradation is random because the primary act of light absorption by the carbonyl is itself a random process, as is the location of the carbonyl in the chain. In the absence of the carbonyl groups the polystyrene would decompose very slowly. Our basic assumption then is that the presence of the carbonyl at the levels used (1 and 2%) will not significantly affect the solution properties of polystyrene. Obviously for a polymer which is already significantly photodegradable, no other monomer need be incorporated and this assumption would not be required.

Figure 2 illustrates the changes which occur in the molecular weight distribution of these polymers after photodegradation in butyl acetate solvent as a function of the irradiation time. The distributions were determined by gel permeation chromatography using the same solvent in order that they could be injected directly onto the column. Dispersities ($\overline{M}_w/\overline{M}_n$) were then calculated from the GPC curves.

The initial dispersity of 1.57 for PS-MVK-1 is in good agreement with the expected value for bulk polymerization initiated by monoradicals and terminated predominantly by coupling. It is analogous to condensation polymerization wherein two chains ($f = 2$) have grown independently and mutually couple to terminate. In this case it has been shown[10] that the dispersity is given by

$$\bar{\chi}_w/\bar{\chi}_n = 1 + (1/f) = 1.5 \qquad (5)$$

where $\bar{\chi}_w$ and $\bar{\chi}_n$ are weight and number average degrees of polymerization, respectively. The dispersities obtained for PS-MVK-1 and PS-MVK-2 as a function of irradiation time are plotted in Figure 3.

It can be seen that both polymers rapidly approach a dispersity of 2.0 after about 1 h of irradiation, thus confirming theoretical predictions. Whereas PS-MVK-1 reaches this value and maintains it even after 20 h of irradiation, PS-MVK-2 only approaches the theoretical dispersity. This is obviously a consequence of the broad initial molecular weight distribution of the latter polymer. In any case the deviation from the theoretical value is only of the order of 10%, which is not much greater than that inherent in determining the dispersity from GPC curves. However, in applying this technique it is obviously better to start with a distribution close to normal, which is usually obtained in bulk or solution polymerization taken to relatively low conversion, as in PS-MVK-1.

Determination of *K* and *a*

To determine the *K* and *a* values for polystyrene in toluene, a solution of the copolymer in toluene is irradiated for various lengths of time. At the end of each period the intrinsic viscosity is determined and a 3 cm^3 aliquot removed for a single point osmotic pressure measurement. Starting with 60 cm^3 of 0.4% solution there is no difficulty in obtaining a dozen or more points in a single experiment. A single point osmotic pressure requires about 15–20 min and the viscometry is facilitated by the automatic viscometer described previously.[7] A complete series can usually be carried out in 1 day.

The osmometry results on irradiated samples of PS-MVK-1 and PS-MVK-2 are illustrated in Figures 4 and 5, respectively.

Table III
Data Used in Calculating Viscosity–Molecular Weight Relationship for PS-MVK-1

Irradiation time, min	$[\eta]$	π/c[a]	$M_n \times 10^{-3}$ [b]	Dispersity[c]	$M_w \times 10^{-3}$ [d]	S[e]
0	0.991	0.22	197	1.57	309	0
3	0.930	0.24	171	1.59	272	0.15
7	0.861	0.27	149	1.62	242	0.32
15	0.756	0.31	120	1.68	201	0.64
30	0.633	0.40	89	1.77	158	1.21
50	0.572	0.45	76	1.85	141	1.59
75	0.468	0.58	58	1.95	112	2.39
100	0.444	0.62	53	2.00	107	2.69
163	0.372	0.77	41.6	2.00	83	3.73
222	0.338	0.86	36.7	2.00	73	4.37
280	0.318	0.93	33.9	2.00	68	4.81
380	0.299	1.00	31.1	2.00	62	5.33
1340	0.264	1.20	25.8	2.00	52	6.63

[a] $c = 0.400$ g dl^{-1}. [b] From osmometry, using single point measurements. [c] From Figure 3. [d] From M_n and dispersity data. [e] Chain breaks per molecule: $S = [\overline{M}_n^0/\overline{M}_n^t] - 1$.

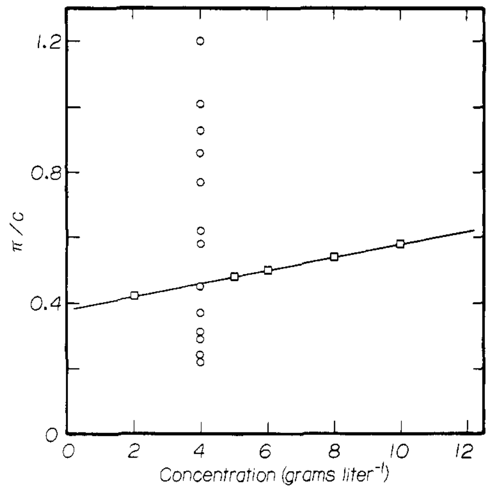


Figure 4. Osmometry data on irradiated samples of PS-MVK-1.

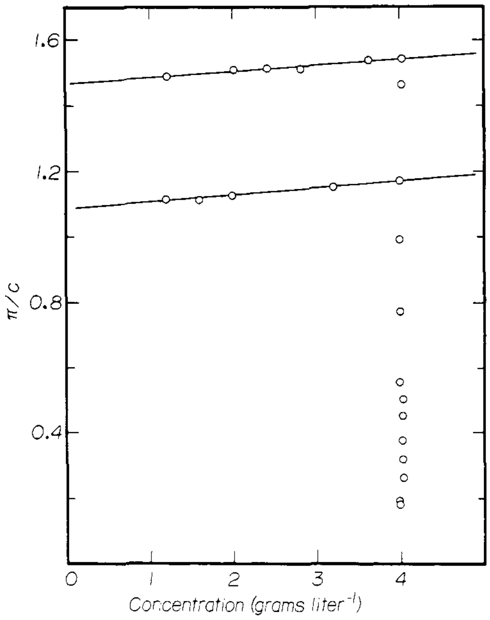


Figure 5. Osmometry data on irradiated samples of PS-MVK-2.

Also shown are the three dilution series listed in Table II which were used in order to determine an average slope of the plot of π/c vs. c. The vertical lines of data points represent the increasing osmotic pressure of samples taken after increasing periods of irradiation. Number average molecular weights of these samples were then determined by linear extrapolation, using the average slope of 0.0195 in order to calculate the $(\pi/c)_0$ intercept. Table III lists the relevant data for PS-MVK-1 with dispersity data estimated from Figure 3.

Double logarithmic plots of intrinsic viscosities vs. number average molecular weights thus determined for both PS-MVK-1 and PS-MVK-2 are shown in Figure 6. It is seen that the plots exhibit considerable curvature in the early stage (upper right portion), but become linear as the distribution approaches the most probable. The two curves are parallel, but do not coincide since PS-MVK-2 does not reach a dispersity of 2.0 because of the very broad initial distribution.

Since the viscosity average molecular weight is normally closer to the weight than the number average, the first-order correction for dispersity can be obtained by calculating $\overline{M}_w$ from the known dispersity. In our procedure, we assume that if we start with a nearly normal distribution such as PS-MVK-1, a polydispersity of 2.0 will be reached after approximately two breaks per number average chain. Regression analysis of the last seven points from Table III, assuming $\overline{M}_w = 2.0\overline{M}_n$, gives the solid line shown in Figure 7. The dashed line in Figure 7 corresponds to the relation obtained by Oyama[11] for polystyrene in toluene also at 30 °C and is in excellent agreement with our results. Furthermore, the points in Figure 7, which are all of the values obtained in the experiment corrected for dispersity as determined by GPC, also lie very close to both lines. Our data give $K = 9.0 \times 10^{-5}$ and $a = 0.73$ as compared to $K = 12.0 \times 10^{-5}$ and $a = 0.71$ for Oyama's relation. The error in the calculated $\overline{M}_w$ from the two relations is less than 10%, which is certainly satisfactory for most practical purposes.

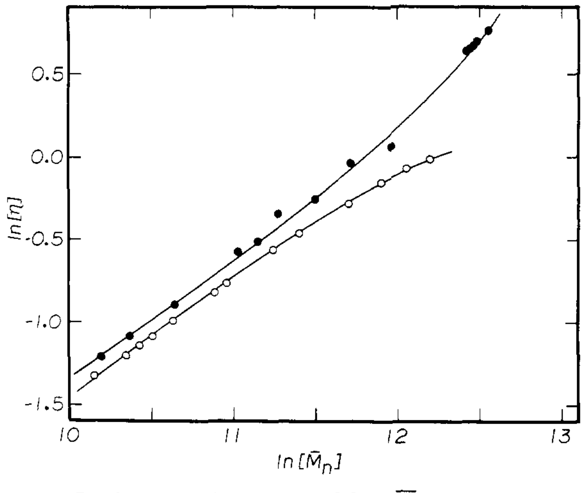


Figure 6. Double logarithmic plot of $[\eta]$ vs. $\overline{M}_n$ for (○) PS-MVK-1 and (●) PS-MVK-2.

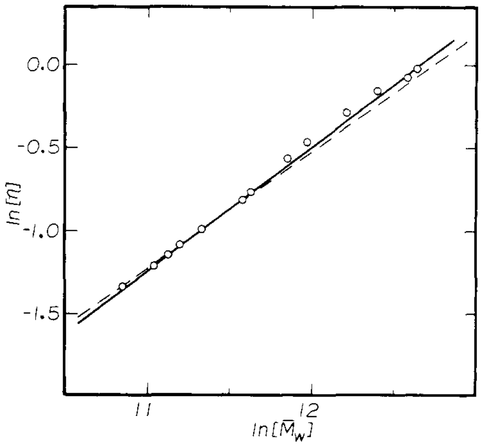


Figure 7. Double logarithmic plot $[\eta]$ vs. $\overline{M}_w$ for PS-MVK-1: (○) experimental points adjusted to $\overline{M}_w$ basis; (—) line based on regression analysis of last seven points; (- - -) line based on relationship obtained from ref 11.

Now that a value for a has been estimated we can test the data from PS-MVK-2, by correcting for the observed polydispersity and calculating $\overline{M}_v$ from eq 4. Figure 8 shows the $\ln[\eta]$ vs. $\ln[\overline{M}_v]$ relation calculated from our K and a values, along with the data on PS-MVK-2 corrected for dispersity. It is evident that the points now fit the theoretical line within experimental error. Clearly if one had independent data on the breadth of the distribution of the degraded samples it would not be necessary to start with a nearly normal initial distribution in order to obtain satisfactory values of K and a. In most cases such data are not available and are difficult to obtain, hence it is best to start with a distribution in the starting copolymer as close to normal as possible.

The correspondence between K and a values given here and literature data suggests that the presence of small amounts

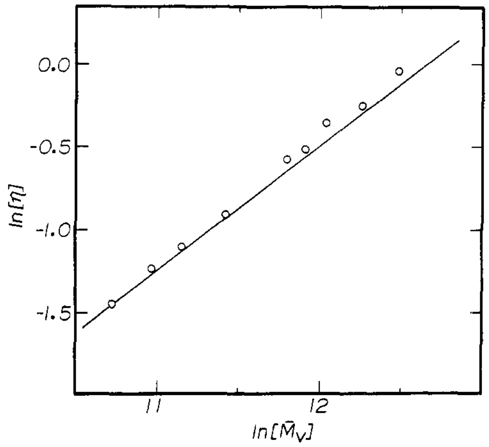


Figure 8. Double logarithmic plot of [η] vs. $\bar{M}_v$ for PS-MVK-2: (●) experimental points adjusted to $\bar{M}_v$ basis; (—) line based on K, a values as determined for PS-MVK-1.

of vinyl ketone units in the polystyrene chain does not affect the Mark–Houwink parameters significantly, and leads to speculation that the procedure described has some general validity. Furthermore it is worth pointing out that it is not essential to use a mercury lamp to induce photodegradation. As has been well established in previous studies from these laboratories, nearly any polymer containing vinyl ketone groups will undergo random scission in solution when exposed to near-uv radiation.

The degradation could easily be carried out by simply exposing an oxygen-free solution to normal solar radiation in a Pyrex flask. Other chemical or physical processes leading to random scission of polymer chains could also be used, provided that they do not lead to extensive chemical changes in the system under study.

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Calculation of Accuracy and Correction Factors in the Viscometric Determination of Chain Scission in Polymers

Thomas L. Nemzek and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.
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ABSTRACT: A computer modeling study has been made of the degradation of polymer systems whose molecular weight distributions are given by either the Schulz distribution or by sums of Flory distributions. The calculations considered degradation by random scission only. The purpose of the study was to evaluate the applicability of equations for estimating the quantum yield of chain scission from changes in the weight average or viscosity average molecular weights. It was found that the error involved in using these equations could be greater than 20% if the initial dispersity, γ_0, did not fall in the range $1.5 < \gamma_0 < 2.5$ but could be estimated if the initial molecular weight distribution was known. Procedures are described for correcting viscometric data to provide accurate quantum yields and scission rates when the initial molecular weight distribution has been determined.

Viscometry is a convenient method for studying the random photodegradation of polymers in solution. The parameter of interest in such a study is the quantum yield of chain scission, ϕ_s, defined by

$$\phi_s = S_n/I_{abs}$$

$$S_n = \frac{W}{M_n(0)}\left(\frac{M_n(0)}{M_n(\tau)} - 1\right) \qquad (1)$$

where S_n is the number of moles of chain breaks, I_{abs} is the number of moles of photons absorbed, W is the total weight of polymer in solution, $M_n(0)$ is the initial number average molecular weight, and $M_n(\tau)$ is the number average molecular weight after an amount of irradiation such that the probability of rupture at a given monomer unit is equal to τ. Note that to determine ϕ_s one needs number average molecular weights as a function of irradiation, whereas viscosity measurements yield the viscosity average molecular weight, M_v, which lies between M_n and the weight average molecular weight, M_w, and is usually closer to the latter. Amerik and Guillet[1] degraded copolymers of methyl methacrylate and methyl vinyl ketone, as well as calculating molecular weight averages for the degradation of sums of Flory distributions. They concluded that, within experimental error, one could approximate S_n by S_w, where

$$S_w = \frac{2W}{M_w(0)}\left(\frac{M_w(0)}{M_w(\tau)} - 1\right) \qquad (2)$$

In order to apply this equation, one must first assume that the molecular weights determined from viscosity data are approximately equal to the weight average molecular weights.

The model degradation calculations of Amerik and Guillet were done for distributions whose initial dispersities, γ_0,

$$\gamma_0 = M_w(0)/M_n(0) \qquad (3)$$