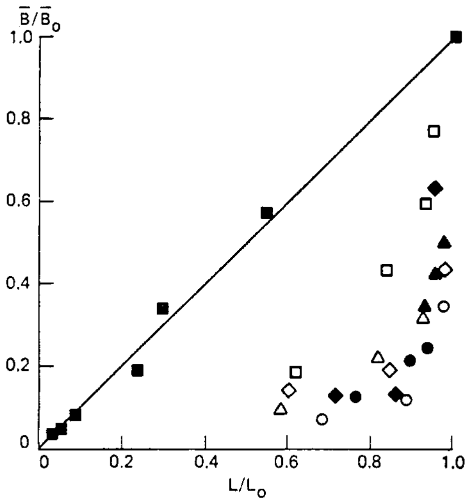

Figure 1. Effect of fraction of light absorbed (L/L_0) by the polymer (polypropylene film) containing ultraviolet stabilizers on the fraction of bonds broken/polymer molecule ($\bar{B}/\bar{B}_0$) for polymer films containing the following ultraviolet light stabilizers: control films with external filters (■), nickel bis(dibutyldithiocarbamate) (○), 2,4-di-*tert*-butyl-6-(5-chloro-2*H*-benzotriazol-2-yl)phenol (△), [2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolato]]nickel (▲), zinc bis(dibutyldithiocarbamate) (□), 4-(dodecyloxy)-2-hydroxybenzophenone (●), 4,4′-bis(octyloxy)-2-hydroxybenzophenone (◇), and bis(2′-hydroxy-5′-methyllaurophenone oximato)nickel(II) (◆).

the quantitative calculation of the importance of screening and NSP. Furthermore, the relative importances of screening and NSP depend on the concentration of the stabilizer. As the concentration of a stabilizer increases, the depth of penetration of the incident light into the polymer decreases; hence, the screening process increases in importance.

In conclusion, all of the ultraviolet stabilizers tested act as ultraviolet screens and through NSP. The method presented here for determining the relative importance of screening and NSP should be useful in other polymer–stabilizer systems.

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Upper Molecular Weight Limit for the Characterization of Polystyrene in Gel Permeation Chromatography

E. L. SLAGOWSKI, L. J. FETTERS,* and
DONALD MCINTYRE

*Institute of Polymer Science, The University of Akron,
Akron, Ohio 44325.* *Received January 14, 1974*

Gel permeation chromatography (GPC) is a widely used tool for characterizing polymeric materials.[1] However, because of the lack of adequate polymer standards, there has been no attempt using such materials to determine, experimentally, the maximum size that current GPC columns can resolve. It is well known that many commercially available polymers have very high molecular weight tails. Also, recent work has shown[2] that very high molecular weight polystyrene, having molecular weights greater than 5×10^6 g/mol, can be made. Consequently the validity of characterizing this range of molecular weights by GPC must be tested. It will be shown in this work that the failure of current GPC columns to resolve high molecular weight polymers is primarily due to shear degradation of the polymer either in the column or in the associated plumbing.

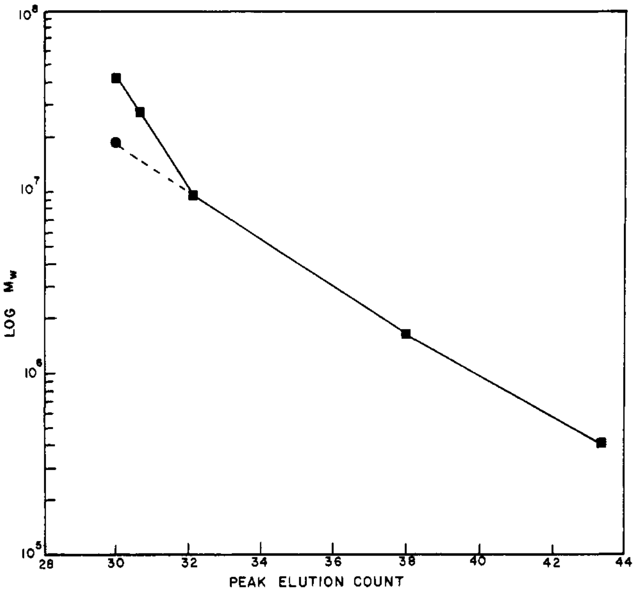

Figure 1. Calibration curve of weight-average molecular weight against peak elution count: (■) molecular weight of sample measured before being put in GPC columns; (●) molecular weight of sample measured after elution through GPC columns.

Experimental Section

Polymer Synthesis. The synthesis of the highest molecular weight polystyrenes (LJF-13 and LJF-18) was accomplished with the aid of a high-vacuum apparatus. The basic details of the use of this equipment have appeared elsewhere.[3,4] Since the attainment of the ultra-high molecular weight polystyrenes requires an extremely low concentration of initiator (10^{-6} to 10^{-7} *M*), precautions must be taken which will ensure the removal of virtually all terminating impurities. To this end a benzene solution[5] of (*sec*-butyl) (*n*-butyl) Mg was used to purify the monomer and also to simultaneously purge the reactor, solvent, and monomer prior to the addition of the initiator.

The solvent used for these polymerizations was tetrahydrofuran, which was purified in the conventional manner.[3,4] The "initiator" was low molecular weight polystyryllithium in benzene prepared by reacting *sec*-butyllithium with styrene.

The polymerization reactor was a 1-l. flask to which was attached another flask of identical size. Following the distillation of the monomer (about 20 g) and solvent (total volume 0.6–0.7 l.), the reactor was sealed off from the vacuum line. When the solution was at room temperature a dilute benzene solution of dibutylmagnesium was added and the mixture was allowed to stand for 1 hr or so. Then the mixture was transferred to the attached 1 l. flask and the solvent and monomer were distilled back into the reactor. This step was repeated at least five times in order to rinse the reactor free from the dibutylmagnesium. It should be mentioned that this organometallic does not cause any significant polymerization of the styrene during this purification procedure.

When the final transfer of the monomer and solvent was achieved, the mixture was frozen with liquid nitrogen and the second flask was removed by sealing off at the glass constriction used to attach the two flasks, one to the other. The mixture was thawed and the dilute initiator solution was added. Since tetrahydrofuran was the solvent, the polymerization was completed in several minutes. The very low chain-end concentration used

Table I
Molecular Constants for High Molecular Weight Polystyrenes[9]

Sample No.	$M_w \times 10^{-6}$ [a] g/mol	$M_z \times 10^{-6}$ [b] g/mol	$[\eta]$,[c] dl/g	Peak Retention Count
LJF-13	43.7 ± 0.2	48.8 ± 5.5	65 ± 2	30
LJF-18	27.3 ± 0.5	31.8 ± 2.6	36.5 ± 0.1	30.7
D-I-1-1	9.6 ± 0.6	11.2	14.4 ± 0.1	32.1
W.A. 61970	1.68 ± 0.04	1.89 ± 0.01	3.86 ± 0.02	38.0
W.A. 25166	0.411 ± 0.001	0.450	1.37 ± 0.02	43.4

[a] Averaged molecular weights from light scattering and sedimentation equilibrium. [b] Molecular weights determined by sedimentation equilibrium. [c] Measured in tetrahydrofuran at 30° with a low shear viscometer.

meant that these polymerizations could be carried out at 25° without the development of an uncontrollable exotherm.

(It should be mentioned that the unsubstantiated claim[6] has been made, and accepted,[7] that even with the most vigorous of purification procedures, the residual concentration of reactive impurities in these anionic polymerization systems is about 3 × 10^{-6} *M*. Since the chain-end concentration used in this work is less than this proposed threshold impurity level, it is quite obvious that with the appropriate purification techniques, the concentration of reactive impurities can be reduced far below the value given in ref 6.)

The high molecular weight polystyrene designated D-I-1-1 is a high fraction of a polystyrene thermally polymerized at room temperature. The lower molecular weight samples are anionically polymerized polystyrene standard samples from Waters Associates.

Characterization. The Waters Associates Ana-Prep GPC instrument was used in the analytical mode with tetrahydrofuran (Matheson, Coleman & Bell, reagent grade) at 25° as the carrier solvent at a flow rate of 1 ml/min. The porosity and sequence of the five columns of commercial Styragel are: (1) >5 × 10^6, (2) 7 × 10^5 to 5 × 10^6, (3) 7 × 10^5 to 5 × 10^6, (4) 1.5 × 10^5 to 7 × 10^5, (5) 5 × 10^4 to 1.5 × 10^5 Å. This particular column sequence had a plate count of 720 PPF when *o*-dichlorobenzene was the solute and the standard procedure was followed.[8] Samples were prepared on a weight-to-volume basis. Each sample was run at several concentrations and the peak positions used to construct the calibration curve were obtained by extrapolating the peak positions for each sample to zero concentration. This was done in an attempt to eliminate the effect of solution viscosity on the chromatogram. The peak positions as a function of concentration did fall on a straight line for all samples where concentration effects were evident. At these concentrations (>0.001 g/ml) the peak position of WA 25166 was not affected by sample loading. Full loop injections were used for all solutions. A siphon with a 5-ml capacity was used.

Results

The peak retention volumes of the polystyrene samples determined in the above manner are given in Table I along with their respective molecular weights. (The exact experimental details pertaining to the characterization and calibration procedures are given in ref 9.) The conventional plot of log *M* *vs.* elution count is shown in Figure 1 and is definitely nonlinear. Semilog plots of $\langle S^2 \rangle$ or $M[\eta]$ *vs.* elution count are similarly nonlinear.

(It should be noted that the molecular weight determined for the W.A. 61970 polystyrene standard sample is not in agreement with the value of 2.1 × 10^6 supplied with this material. However, good agreement was found for the W.A. 25166 sample.)

Our experience in working with five-column systems for lower molecular weight ranges indicates that the exclusion limits are generally about 20 counts. Thus, with the highest molecular weight sample eluting at 30 counts, it would seem that the exclusion limits of this five-column set has not been reached. Consequently, a search was made to determine the cause of this apparent failure of the conventional calibration curve, since the nonlinear portion is well beyond the column exclusion limit.

Table II
Summary of Viscosity Data in Tetrahydrofuran at 30°

Sample	Concn (g/ml), × 10^6	η_{rel}	η_{sp}/c
Diluted master	10.2	1.065_3	64
GPC eluent	9.05	1.022_4	24.8[a]
GPC eluent	9.42	1.024_9	26.4[a]

[a] Average η_{sp}/c = 25.6 ± 0.8, which approximately corresponds to a M_v of 1.9 × 10^7 g/mol (obtained from Mark–Houwink–Sakurada plot[9]).

Polystyrene polymers having molecular weights greater than 10^7 g/mol are known to shear degrade.[2,9] Polystyrene (LJF-13) was therefore rerun in the GPC instrument under such conditions that the entire eluent could be collected and analyzed for molecular weight changes. A portion of the master solution (3.16 × 10^{-4} g/ml) of LJF-13 was injected into the GPC system and the eluent corresponding to the entire area of the polymer distribution trace was collected in a graduated cylinder. This volume included 5 ml of eluent before the appearance of the sample curve plus 5 ml after reaching base-line conditions. The concentration was calculated from expected overall dilution of the original 2-ml sample in the column. The relative viscosity of the collected eluate was measured in a low shear viscometer,[9] for two replicate GPC runs, at 30°. In addition, another solution of master concentration serving as a control standard was diluted to the concentration of the GPC eluent. Its relative viscosity was then determined. The results are shown in Table II.

The actual $[\eta]$ for this polymer is 65 dl/g. If an assumption is made that the measured η_{sp}/c at these low relative concentrations is equivalent to the $[\eta]$ value (the actual error is ~2%), then a M_v may be obtained from the Mark-Houwink-Sakurada plot for this high molecular weight polymer.[9] The calculated M_v for the GPC eluent material based on this assumption is 1.9 × 10^7 g/mol (Table II). The diluted master sample that was not passed through the GPC gave a η_{sp}/c near the true $[\eta]$ value. When this new molecular weight is assigned the sample at the given elution peak, the calibration curve shown as a dotted line in Figure 1 does become linear.

It should also be noted that samples LJF-13 and 18 were also run through the Styragel columns at the reduced flow rate of 0.25 ml/min. This was done to ascertain whether the decreased flow rate could sufficiently decrease the shear rates and lessen the shear degradation. No significant changes in the peak counts or in the shapes of the chromatograms could be detected for either of these two samples. This indicates that reducing the flow rates in the conventional ranges does not avoid the problem of shear degradation in GPC.

Conclusions

We have shown that a single pass through the GPC seriously degrades a 4.37 × 10^7 g/mol of polystyrene by a twofold factor. Therefore any calibration curve obtained from high molecular samples will not be linear. The nonlinearity is not due to exclusion limits of the columns, but represents the use of the undegraded, and therefore untrue, molecular weight. Since the degraded molecular weight of 1.9×10^7 g/mol makes the calibration curve linear, it suggests that polystyrenes of molecular weight greater than about 10^7 g/mol degrade under normal conditions.

Consequently, it must be emphasized that the use of GPC for determining molecular weights when there is a high molecular weight tail in the distribution curve may be seriously in error.

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Communications to the Editor

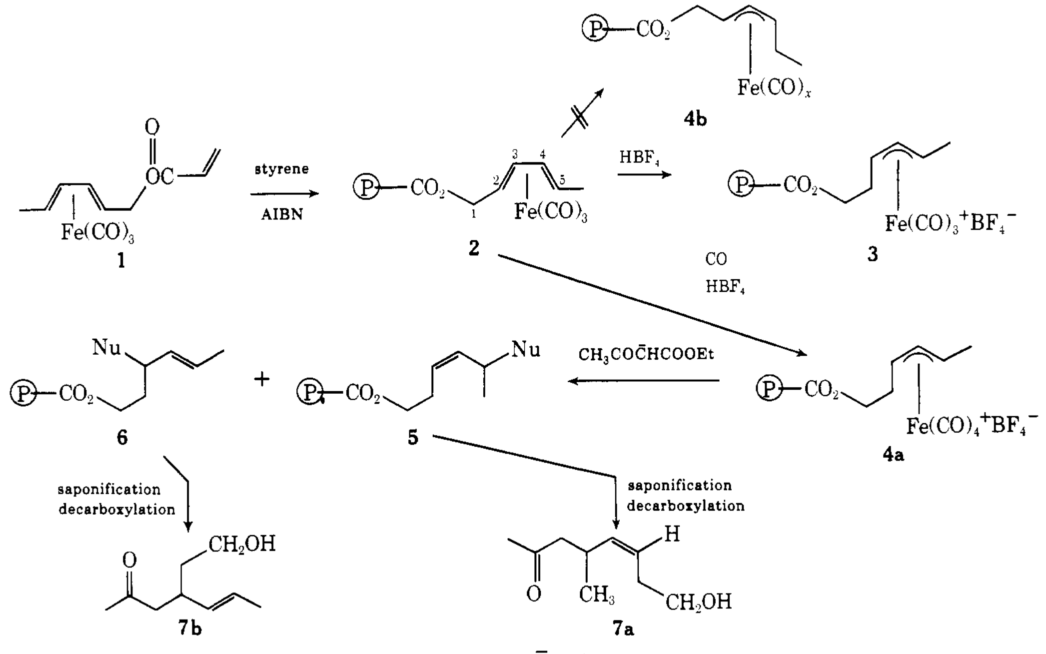
Functionalization of Polymers *via* π-Allyliron Tetracarbonyl Cations

Preliminary studies, reported herein, describe a novel pathway for the functionalization of polymers. We previously reported that η^4-(2,4-hexadienyl acrylate)tricarbonyliron (1) (Scheme I) readily homopolymerized and copolymerized with styrene, methyl acrylate, acrylonitrile, or vinyl acetate.[1] This η^4-(diene)tricarbonyliron function is readily converted in high yield to a polymer-bound π-allyliron tricarbonyl cation, **3**, in the presence of HBF_4[2] or in the presence of both HBF_4 and CO (in CF_3CO_2H) to a polymer-bound π-allyliron tetracarbonyl cation, **4**.[3] The π-allyliron tetracarbonyl cation sites react readily with nucleophiles such as triphenylphosphine or the anion of ethyl acetoacetate to give the 1,4-addition products of the diene moiety.

Protonation of the dieneirontricarbonyl moieties of **2** takes place predominately at C-2 to give **4a** and not **4b**.[4] Treatment of this polysalt with the anion of ethyl acetoacetate gave a mixture of the polymer-bound keto esters **5** and **6**. Their identity was indirectly determined by saponification followed by decarboxylation of the cleaved saponification products to give **7a** and **7b** in a ratio of 4.5 to 1.[5] Thus, predominant attack of the nucleophile on **4a** takes place to give the cis product **5**. In addition to a propensity for cis double bond formation, the nucleophile attacks predominantly at the allyl site farthest from the polymer backbone. This might be a steric effect since both allylic positions are secondary.

These studies parallel the recent report by Whitesides *et al.*[6] of the specific synthesis of allyl species containing a cis double bond from π-allyliron tetracarbonyl cations. On nucleophilic attack, the cis product was formed even when there is a choice between cis and trans double-bond formation.[6,7] That report prompts our description of simi-

Scheme I



Nu = $CH_3CO\bar{C}HCOOEt$