

# Investigation of the Dependence of the Infrared Absorptivity of a Functional Moiety on the Molecular Weight of a Homopolymer

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## Synopsis

The subject of this investigation was the determination of the effect of molecular weight (MW) on the infrared absorptivity of a functional moiety in polystyrene homopolymer. It was found that no consistent dependence of infrared absorptivity on MW was found for two sharp absorptions of polystyrene across the MW range from 600 to  $2 \times 10^6$ . It was shown that end group effects for the very-low-molecular-weight polymer fraction may be subtle and should be accounted for when using homopolymer calibration standards in the study of the dependence of copolymer composition on MW.

## INTRODUCTION

In earlier work<sup>1-7</sup> the composition of copolymers was studied as a function of molecular weight (MW). A tacit assumption in all work of this type was that the absorbance of a specific functional group was essentially independent of the MW of the molecule in which the functional group resided. This assumption is ordinarily very difficult to test for the homopolymers that are used as calibration standards to determine the copolymer composition, since a set of narrow MW polymer standards covering a wide range of MW is rarely available for the various homopolymers of the monomers incorporated into the copolymers under investigation.

Further, the determination of the effect of MW on absorbance of a specific functional group in a copolymer is far more difficult than for a homopolymer, due to the lack of copolymer MW standards.

The need to determine if such a MW effect on absorbance exists is indicated by the dependence of the differential refractive index on MW of polyethylene solutions.<sup>8</sup> Further, the results of Hamielec<sup>9</sup> showed that the ultraviolet absorbance of a functional group was dependent on the composition of the copolymer in which it resided; i.e., cell path length and total concentration of the functional group were held constant. The subject of the present investigation was the determination of the effect of MW on the absorptivity of a functional moiety in a homopolymer, since a set of copolymer MW standards is not available.

Polystyrene was chosen for this study since a set of narrow MW standards covering a wide range of MW was available. Two infrared absorptions were studied. These were two intense, relatively sharp absorptions at  $1493 \text{ cm}^{-1}$  ( $6.698 \mu\text{m}$ ) and  $1450 \text{ cm}^{-1}$  ( $6.896 \mu\text{m}$ ). The absorption at  $1493 \text{ cm}^{-1}$  has been assigned to one mode of vibration of the benzene ring alone, while the absorption

at  $1450\text{ cm}^{-1}$  has been assigned to a combination of the bending mode of the methylene group and one mode of vibration of the benzene ring.<sup>10</sup> Investigation of possible dependence of the absorptivity of these infrared bands on the MW of the polystyrene molecule in which they reside was done as a first step in determining if such dependence exists and the magnitude of such dependence.

These polystyrene standards were anionically polymerized using *n*-butyllithium initiator in benzene<sup>11</sup> and thus yield atactic polymers.<sup>12</sup> Therefore, no effects due to stereoregularity were expected on the infrared spectra.

## EXPERIMENTAL

The polymer standards used in this study were narrow polystyrene standards supplied by ARRO Laboratories, Joliet, IL. The nominal molecular weights used were as follows:  $2 \times 10^6$ ,  $\overline{M}_w/\overline{M}_n < 1.30$ , Cat. No. 500-28;  $4.98 \times 10^5$ ,  $\overline{M}_w/\overline{M}_n < 1.10$ , Cat. No. 500-20A;  $3.70 \times 10^4$ ,  $\overline{M}_w/\overline{M}_n < 1.06$ , Cat. No. 500-14A;  $2.10 \times 10^3$ ,  $\overline{M}_w/\overline{M}_n < 1.10$ , Cat. No. 500-6; and  $6.00 \times 10^2$ ,  $\overline{M}_w/\overline{M}_n < 1.10$ , Cat. No. 500-2. Solutions were prepared by individual weighing of each concentration. Solutions were established by shaking 30 min at room temperature. The solvent used was tetrachloroethylene (TCE) supplied by Eastman Organic Chemical Co., Cat. No. 2418. Infrared absorptions were determined on a Perkin-Elmer 457 grating infrared spectrometer, Perkin-Elmer Co., Norwalk, CT, using 1.00-mm pathlength NaCl cells, Cat. No. 006-7006, supplied by Wilks Co., So. Norwalk, CT, and 0.13-mm cells constructed in-house. The infrared spectrometer was adjusted according to the manual before each experiment. The results were checked by repeating the infrared scans on a Perkin-Elmer model 221 prism infrared spectrometer, with the following conditions: scan drive, 1; scan time, 32 min; suppression, 0; expansion, 1 $\times$ ; amplifier gain, 4; slit program, 940; and source amperage, 0.8.

Experiments were done with a solvent reference of equal pathlength in each case. Five solution concentrations were run at each of the five molecular weights of the polystyrene. Infrared absorptions were measured at  $1493$  and  $1450\text{ cm}^{-1}$ . Scans were made from  $1700\text{ cm}^{-1}$  ( $5.88\text{ }\mu\text{m}$ ) to  $1350\text{ cm}^{-1}$  ( $7.41\text{ }\mu\text{m}$ ) for each solution to establish a baseline.

The experimental error for the replicate determination of absorbance of a solution was found to be  $\pm 0.005$  absorbance units.

## RESULTS AND DISCUSSION

The infrared absorbances (*A*) for each MW polystyrene are presented in Table I for the 1.00-mm pathlength cell (for the  $1493$  and  $1450\text{ cm}^{-1}$  absorptions) and in Table II for the 0.13-mm pathlength cell for the  $1493\text{ cm}^{-1}$  absorption. The data for all MW for the  $1493\text{ cm}^{-1}$  absorption in the 1.0-mm pathlength cell, for the  $1450\text{ cm}^{-1}$  absorption in the 1.0-mm pathlength cell, and for the  $1493\text{ cm}^{-1}$  absorption in the 0.13-mm pathlength cell are plotted in Figures 1-3, respectively. Table III presents the slope, intercept, and overall standard deviation from the linear least-squares data fit for each MW and for all MW combined, at the two wavelengths for the 1.00-mm cell and at one wavelength for the 0.13-mm cell.

Figures 1-3 also show the linear least-squares fit to all 25 data points in each case and the overall standard deviation of the linear least-squares fit to the data.

TABLE I  
Infrared Absorbance of Polystyrene in TCE in the 1.0-mm Pathlength Cell

Polystyrene MW	Concentration, g/l.	Infrared absorption	
		1493 $\text{cm}^{-1}$	1450 $\text{cm}^{-1}$
$2.0 \times 10^6$	0.477	0.033	0.022
	1.000	0.075	0.061
	2.511	0.193	0.172
	4.018	0.306	0.282
	5.566	0.429	0.391
$4.98 \times 10^5$	0.520	0.049	0.057
	1.000	0.073	0.087
	2.529	0.187	0.178
	3.946	0.298	0.280
	5.534	0.413	0.394
$3.7 \times 10^4$	0.489	0.044	0.040
	1.074	0.080	0.070
	2.474	0.197	0.180
	4.030	0.302	0.290
	5.453	0.404	0.382
$2.1 \times 10^3$	0.522	0.046	0.032
	1.029	0.080	0.067
	2.540	0.191	0.164
	4.035	0.290	0.291
	5.545	0.402	0.367
$6.0 \times 10^2$	0.537	0.038	0.033
	1.092	0.074	0.074
	2.490	0.169	0.170
	3.975	0.272	0.275
	5.578	0.382	0.395

Inspection of Figure 2 shows that, aside from some apparently random scatter of three data points, the data fall within the standard deviation interval of the least-squares fit for the entire MW range. This indicates that at 1450  $\text{cm}^{-1}$  absorptivity remains constant independent of MW. Inspection of Figures 1 and 3, which refer to the absorption at 1493  $\text{cm}^{-1}$ , show that the data generally fall within the standard deviation interval of the least-squares fit for the majority of the MW range. However, the 600-MW polystyrene has consistently lower absorbance than the rest of the polystyrene MW standards in both Figures 1 and 3. The results in Figures 1 and 2 were rechecked by running the solutions on another infrared spectrometer (Perkin-Elmer model 221). The new results obtained were essentially identical. This indicates a decrease in the absorptivity at 1493  $\text{cm}^{-1}$  of the 600-MW standard relative to the other standards, while no such decrease was observed at 1450  $\text{cm}^{-1}$ .

The linear least-squares data in Table III were used to make calculations comparing the calibration line for the 600-MW standard and the calibration line for all 25 data points for the 1493  $\text{cm}^{-1}$  absorption in the 1.00-mm cell. These calculations showed that the calibration line for the 600-MW standard yielded 7–15% lower absorbance over the concentration range of 0.5–5.0 g/l. than the

TABLE II  
Infrared Absorbance of Polystyrene in TCE in the 0.13-mm Pathlength Cell

Polystyrene MW	Concentration, g/l.	Infrared absorbance at 1493 cm <sup>-1</sup>
2.0 × 10 <sup>6</sup>	4.660	0.058
	8.638	0.087
	16.588	0.179
	28.272	0.284
	40.036	0.386
4.98 × 10 <sup>5</sup>	4.408	0.075
	8.432	0.106
	16.570	0.192
	28.170	0.258
	39.940	0.402
3.7 × 10 <sup>4</sup>	4.448	0.050
	8.670	0.093
	16.384	0.180
	28.028	0.320
	39.288	0.400
2.1 × 10 <sup>3</sup>	4.182	0.047
	8.554	0.091
	15.912	0.165
	29.200	0.292
	39.892	0.380
6.0 × 10 <sup>2</sup>	3.570	0.035
	8.610	0.091
	15.508	0.155
	27.724	0.256
	40.430	0.365

calibration line for all 25 data points. This would yield a significant effect on a calculation of copolymer composition versus MW.

This observed decrease in absorbance at 1493 cm<sup>-1</sup> while no decrease was observed at 1450 cm<sup>-1</sup> might superficially appear confusing. However, it is caused by an end group effect. The polystyrene standards used are prepared with *n*-butyllithium initiator and terminated with a proton donor.<sup>11</sup> The *n*-butyl end group becomes significant in its effect only with the short-chain 600-MW standard. The magnitude of this effect can be approximated by assuming that the 600-MW standard is composed of exactly six styrene units. Addition of an *n*-butyl end group decreases the concentration of phenyl groups by 6.2% and increases the concentration of methylene groups by 5.0%.

Since the 600-MW standard is not monodisperse as to MW, these calculations are only approximate. However, the *n*-butyl end group would be expected to decrease the absorbance at 1493 cm<sup>-1</sup> since it is assigned to one mode of vibration of the benzene ring. The absorbance at 1450 cm<sup>-1</sup> is assigned to a combination of the bending mode of the methylene group and one mode of vibration of the benzene ring and would be expected to simultaneously increase and decrease

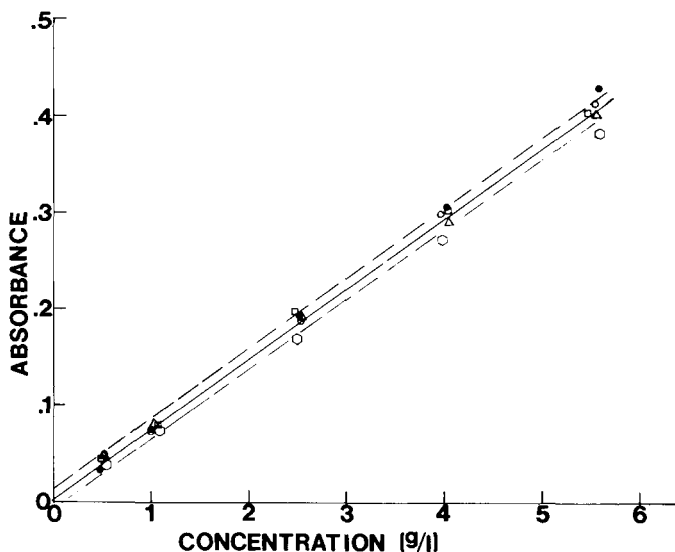


Fig. 1. Infrared absorbance at  $1493\text{ cm}^{-1}$  vs. concentration of polystyrene in tetrachloroethylene in a 1.00-mm pathlength cell: (—) linear least-squares fit to all points; (---) overall standard deviation of least-squares fit; (●) PS standard  $2.0 \times 10^6$ ; (○) PS standard  $4.98 \times 10^5$ ; (□) PS standard  $3.7 \times 10^4$ ; (Δ) PS standard  $2.1 \times 10^3$ ; (○) PS standard  $6.0 \times 10^2$ .

by the addition of the *n*-butyl end group. It is thus not surprising that the absorbance at  $1450\text{ cm}^{-1}$  is the same for the 600-MW standard as for the higher MW standards.

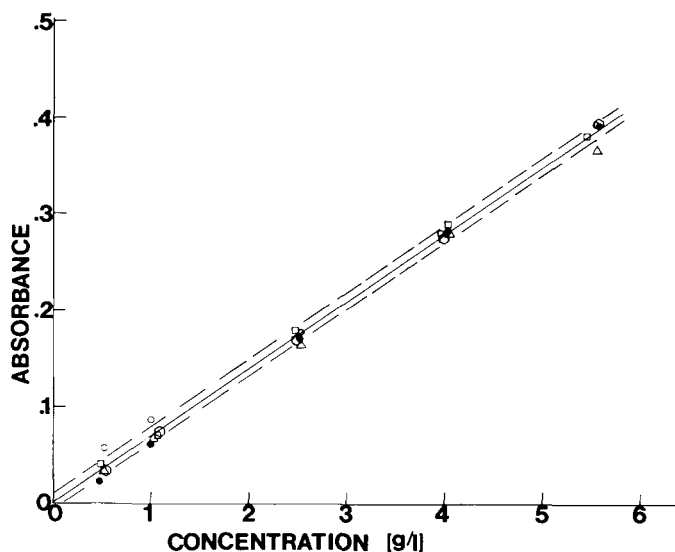


Fig. 2. Infrared absorbance at  $1450\text{ cm}^{-1}$  vs. concentration of polystyrene in tetrachloroethylene in a 1.00-mm pathlength cell: (—) linear least-squares fit to all points; (---) overall standard deviation of least-squares fit; (●) PS standard  $2.0 \times 10^6$ ; (○) PS standard  $4.98 \times 10^5$ ; (□) PS standard  $3.7 \times 10^4$ ; (Δ) PS standard  $2.1 \times 10^3$ ; (○) PS standard  $6.0 \times 10^2$ .

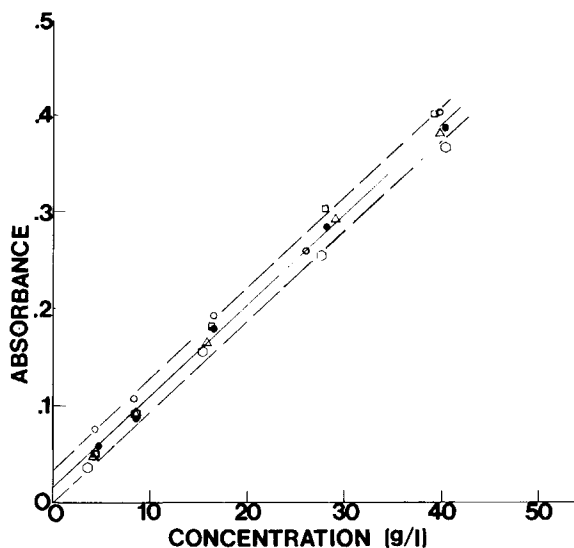


Fig. 3. Infrared absorbance at  $1493\text{ cm}^{-1}$  vs. concentration of polystyrene in tetrachloroethylene in a 0.13-mm pathlength cell: (—) linear least-squares fit to all points; (---) overall standard deviation of least-squares fit; (●) PS standard  $2.0 \times 10^6$ ; (○) PS standard  $4.98 \times 10^5$ ; (□) PS standard  $3.7 \times 10^4$ ; (Δ) PS standard  $2.1 \times 10^3$ ; (○) PS standard  $6.0 \times 10^2$ .

TABLE III  
Slope, Intercept, and Overall Standard Deviation from the Linear Least-Squares Fit

Polystyrene MW	Slope	Intercept	Overall standard deviation of linear least-squares fit
$1493\text{ cm}^{-1}$ , 1.00-mm Cell			
$2.0 \times 10^6$	$7.75 \times 10^{-2}$	$-0.31 \times 10^{-2}$	$1.75 \times 10^{-3}$
$4.98 \times 10^5$	$7.38 \times 10^{-2}$	$0.44 \times 10^{-2}$	$5.41 \times 10^{-3}$
$3.7 \times 10^4$	$7.31 \times 10^{-2}$	$0.77 \times 10^{-2}$	$6.21 \times 10^{-3}$
$2.1 \times 10^3$	$7.07 \times 10^{-2}$	$0.86 \times 10^{-2}$	$2.99 \times 10^{-3}$
$6.0 \times 10^2$	$6.84 \times 10^{-2}$	$-0.005 \times 10^{-2}$	$1.16 \times 10^{-3}$
All 25 points	$7.27 \times 10^{-2}$	$0.35 \times 10^{-2}$	$10.7 \times 10^{-3}$
$1450\text{ cm}^{-1}$ , 1.00-mm Cell			
$2.0 \times 10^6$	$7.28 \times 10^{-2}$	$-1.17 \times 10^{-2}$	$1.35 \times 10^{-3}$
$4.98 \times 10^5$	$6.71 \times 10^{-2}$	$1.78 \times 10^{-2}$	$6.91 \times 10^{-3}$
$3.7 \times 10^4$	$7.03 \times 10^{-2}$	$0.23 \times 10^{-2}$	$6.29 \times 10^{-3}$
$2.1 \times 10^3$	$6.84 \times 10^{-2}$	$-0.30 \times 10^{-2}$	$12.3 \times 10^{-3}$
$6.0 \times 10^2$	$7.14 \times 10^{-2}$	$-0.58 \times 10^{-2}$	$2.88 \times 10^{-3}$
All 25 points	$7.00 \times 10^{-2}$	$-0.008 \times 10^{-2}$	$9.34 \times 10^{-3}$
$1493\text{ cm}^{-1}$ , 0.13-mm Cell			
$2.0 \times 10^6$	$9.41 \times 10^{-3}$	$1.40 \times 10^{-2}$	$7.88 \times 10^{-3}$
$4.98 \times 10^5$	$8.90 \times 10^{-3}$	$3.30 \times 10^{-2}$	$18.2 \times 10^{-3}$
$3.7 \times 10^4$	$10.4 \times 10^{-3}$	$0.81 \times 10^{-2}$	$15.7 \times 10^{-3}$
$2.1 \times 10^3$	$9.38 \times 10^{-3}$	$1.17 \times 10^{-2}$	$6.01 \times 10^{-3}$
$6.0 \times 10^2$	$8.82 \times 10^{-3}$	$1.14 \times 10^{-2}$	$6.61 \times 10^{-3}$
All 25 points	$9.36 \times 10^{-3}$	$1.58 \times 10^{-2}$	$15.6 \times 10^{-3}$

## CONCLUSIONS

This investigation has shown that apparently no MW dependence of the absorptivity of the  $1450\text{ cm}^{-1}$  absorption exists across the MW range from 600 to  $2 \times 10^6$ . Also, no MW dependence of the absorptivity of the  $1493\text{ cm}^{-1}$  absorption was observed for the MW range from 2100 to  $2 \times 10^6$ . However, a significant decrease in absorptivity of the  $1493\text{ cm}^{-1}$  absorption was observed for the 600-MW polystyrene standard. This was due to an end group effect. The fact that the end group affected the  $1493\text{ cm}^{-1}$  absorption but not the  $1450\text{ cm}^{-1}$  absorption emphasizes the subtlety of such effects.

This study has shown that no consistent dependence of infrared absorptivity on MW was found for two sharp absorptions of polystyrene. It has also shown that end group effects for the very-low-molecular-weight polymer fraction may be subtle and should be accounted for when studying the dependence of copolymer composition on MW. It must be noted that solvent may have an effect on the behavior observed constraining the conclusions to the particular solvent used.

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