Hypochromic Effects in UV Spectra of Polymers in Solution

Bernhard STÜTZEL, Takeaki MIYAMOTO,* and Hans-Joachim CANTOW

*Institut für Makromolekulare Chemie der Universität Freiburg,
D-78 Freiburg, i. Br., Stefan-Meier Str. 31, West Germany.*

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ABSTRACT: The hypochromic effect in the UV spectra of polystyrene and styrene copolymers in solution was investigated in detail. For this purpose, isotactic and syndiotactic-rich polystyrenes as well as their dimer model compounds, 2,4-diphenylpentanes, and styrene-methyl methacrylate copolymers were prepared. UV absorption measurements were carried out in dioxane and tetrahydrofuran at various temperatures. The extinction coefficients of phenyl rings depended not only on the solvent and the temperature but also on the microstructure of the polymers. A discontinuous temperature dependence of the extinction coefficients was observed between 40 and 50°C for homopolystyrenes as well as their dimer model compounds. It was suggested that this might be explained in terms of the rotation of phenyl rings. On the other hand, the hypochromicity in binary copolymers appeared to depend strongly on the sequential arrangement of monomers (the chain architecture and the chemical composition of copolymers). The measured average extinction coefficients were well interpreted by a simple treatment by using triad probability proposed by Harwood. The results were discussed in relation to the UV spectrometer which is being used as an auxiliary detector in gel-permeation chromatography and microcolumn chromatography.

KEY WORDS Hypochromic Effect / UV Spectrum / Extinction Coefficient / 2,4-Diphenylpentane / Polystyrene / Styrene—Methyl Methacrylate Copolymer / Sequential Arrangement /

The quantities of eluted homopolymers in gel-permeation chromatography (GPC) and microcolumn-solubility chromatography (MCC) can be determined through the detection of a single physical value, such as refractive index increment, which is proportional to the concentration of the polymer in the eluent. However, the determination of the chemical composition of a binary copolymer at a certain elution count (*i.e.*, the point-by-point composition) requires another quantity to be specified. This can be performed by using an ultraviolet (UV) detector auxiliarily, so far as the extent of absorption at a certain wavelength is different for the two components of the copolymer.^{1,2}

If the UV extinction coefficient, ϵ , depends solely on the population of the units able to absorb in the copolymer chains, the point-by-point composition can be determined easily with such a dual detector system as mentioned above.

However, it has been observed for binary copolymers that the UV extinction coefficient depends not only on the population of the units able to absorb but also on the sequence length of copolymer chains.^{3,4} Moreover, it has been reported that temperature and steric isomerism also affect the extinction coefficient of UV absorption.^{5,6} In this report detailed studies are made on the various factors which may influence the UV absorption of phenyl rings; *i.e.*, (1) the steric isomerism of polystyrene and its dimer model compound, (2) the temperature, (3) the chain architecture of styrene (ST)—methyl methacrylate (MMA) copolymers (*i.e.*, alternating, random, and block with a fixed composition), and (4) the chemical composition of ST—MMA random copolymers.

EXPERIMENTAL

Materials

A stereoisomeric mixture of the 2,4-diphenylpentane was synthesized according to the method

* Permanent address: *Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.*

of Overberger, *et al.*⁷ Separation of *meso*- and *d,l*-isomer by preparative gas chromatography and characterization by NMR spectroscopy were based on the same procedures as used by Bovey, *et al.*⁸ The purity of *d,l*-isomer was 97% and that of *meso*-isomer was better than 88%.

Isotactic polystyrene was polymerized with $\text{Al}(\text{C}_2\text{H}_5)_3\text{—TiCl}_4$ in heptane at 70°C. The product was extracted with methyl ethyl ketone⁹ and the insoluble fraction used as isotactic sample (I-PS).

The I-PS sample was found to be highly isotactic through comparison of its IR and NMR spectra with those reported for isotactic polymers.^{8,9} The syndiotactic-rich sample (S-PS) was prepared by a radical polymerization technique. The molecular weights of these samples estimated from the maximum peak position in GPC were 20×10^4 and 16×10^4 , respectively.

The alternating ST—MMA copolymer (SM—AL) was polymerized at -78°C with $\text{Al}(\text{C}_2\text{H}_5)_{1.5}\text{Cl}_{1.5}$ in toluene according to the method given by Hirooka, *et al.*¹¹ The block copolymer (SM—Block) was kindly provided by Dr. T. Fukuda—Tanaka, University of Kyoto, the preparation and characterization of which are given in ref 10. Random ST—MMA copolymer samples with different ST contents (coded as SM-series) were supplied by the courtesy of Dr. R. J. Brüssau, BASF AG., Ludwigshafen. These

samples were low conversion products prepared by a radical copolymerization method. All the samples were purified by following the usual procedures. Reactivity ratios were determined by the method of Finemann and Ross¹² and found to be $r_1=0.60$ for ST and $r_2=0.55$ for MMA. Harwood—Ritchey's run number¹³ was calculated from the reactivity ratios and the monomer feed composition data. Table I summarizes the results of characterization of the copolymer samples employed.

Measurements

The UV absorption measurements were carried out in spectrograde tetrahydrofuran and dioxane (Uvasol, E. Merck AG., Darmstadt), by a Zeiss DMR-21 UV Spectrometer. The temperature variation of UV absorption was measured in dioxane solution. The concentrations of ST monomer units in solution were about 5×10^{-3} mol/l. In the following the extinction coefficients are given in l/(mol-styrene unit) cm.

RESULTS AND DISCUSSION

UV Spectra of Polystyrenes and Their Dimer Model Compounds

Figure 1 shows UV absorption spectra of isotactic and syndiotactic-rich polystyrenes and *meso*- and *d,l*-2,4-diphenylpentanes in dioxane at various temperatures. There can be seen absorption peaks and shoulders at about 268(λ_1), 264(λ_2), 261(λ_3), 259(λ_4), and 254(λ_5) nm, as indicated by arrows in Figure 1A. The UV spectra of polymer samples show significant differences, depending on the microtacticity of the polymers. The maximum absorption peaks for I-PS and S-PS are different; absorbance of

Table I. Characterization data of ST—MMA copolymer samples used

Sample	ST, mol%	$M \times 10^{-4a}$	Run number	Triad probability		
				f_{SSS}	f_{MSS}	f_{MSM}
SM-20	22.3	14.0	43.38	0.0007	0.0533	0.9458
SM-30	33.1	14.0	56.40	0.0220	0.2531	0.7252
SM-40	41.0	14.0	61.86	0.0607	0.3712	0.5679
SM-50	50.0	15.0	63.42	0.1339	0.4640	0.4021
SM-60	59.0	15.0	60.37	0.2388	0.4998	0.2614
SM-70	69.2	16.0	50.82	0.4004	0.4647	0.1349
SM-80	79.4	16.0	37.03	0.5879	0.3576	0.0545
SM-90	90.8	16.0	17.92	0.8183	0.1779	0.0097
SM—AL	50.0	40.0	100	0	0	1
SM—Block	48.1	13.5 ^b	0	1	0	0

^a Estimated from the maximum peak position in GPC by using a calibration curve for polystyrenes.

^b Number-average molecular weight by osmometry.

Table II. Wavelength λ and extinction coefficient ϵ at peak and shoulder positions of polystyrenes and their dimer model compounds in dioxane solution at 25°C

Sample	λ , nm			$\epsilon \times 10^{-2}$, l/mol ⁻¹ cm ⁻¹		
	λ_1	λ_3	λ_4	ϵ_1	ϵ_3	ϵ_4
S-PS	268.5	261.5	259	1.557	2.084	2.053
I-PS	268	261.5	259	1.463	2.006	2.021
<i>d,l</i> -isomer	268	261	259	1.675	2.248	2.204
<i>meso</i> -isomer	267.5	260.5	258.5	1.538	2.138	2.167

Ultraviolet Hypochromicity of Polymers

Figure 1. UV absorption spectra of isotactic (I-PS), syndiotactic-rich polystyrene (S-PS), *meso*-, and *d,l*-2,4-diphenylpentanes in dioxane at various temperatures. Figures indicate the measuring temperature.

S-PS takes a maximum value at 261 nm and that of I-PS at 259 nm. A similar deviation is observed also between the dimer model compounds. Table II lists the values of extinction coefficients at about 268, 261, and 259 nm in dioxane solution at 25°C. The extinction coefficients of the isotactic polymer and the *meso*-isomer are smaller than those of the syndiotactic-rich polymer and the *d,l*-isomer, respectively. According to Vala and Rice,¹⁴ this is due to the so-called hypochromic effect caused by the anisotropic effect of phenyl rings. A similar hypochromic effect on the steric isomerism has been observed in the case of poly(methyl methacrylate) (PMMA).^{6b,6c} However, in the case of poly[(+)-2-methyl butyl methacrylate] the extinction coefficient of the isotactic polymer is larger than that of the syndiotactic one.^{6c} The isotactic polymer chain is known to take a certain regular helical conformation even in solution.⁹ Such a helical conformation of the chain seems to play an important role in the UV absorption of the isotactic polymer, since the UV absorption is considered to reflect the local structure of the polymer chain. This explanation, however, is not sufficient in view of the fact that the same effect is observed for our dimer model compounds. Thus, the contribution of the helical conformation to UV absorption would be of minor one, if any. The mutual position in space of adjacent phenyl rings seems to control the extinction coefficient as well as the shape and the form of the absorption spectrum.

Temperature Dependence of Extinction Coefficient

Figure 2 shows the temperature dependences of the extinction coefficients of the isotactic polymer and the *meso*-isomer. The coefficients decrease with increasing temperature. Each curve exhibits a small discontinuity between 40 and 50°C. This phenomenon has been attributed to a certain conformational change of polystyrene in solution.⁵ For example, it has been speculated from light-scattering measurements that the destruction of helical turns in the polymer chain occurs above this temperature range.^{5a} Meanwhile, the measurement of the half-width of the NMR peak of phenyl rings suggests that the temporarily stable structure of

Figure 2. Temperature dependences of extinction coefficients of isotactic polystyrene (○) and *meso*-2,4-diphenylpentane (●). Values described on each curve are wavelength (nm).

Figure 3. Temperature dependences of extinction coefficients of syndiotactic-rich polystyrene (○) and *d,l*-2,4-diphenylpentane (●) at 261 nm.

groups of chain units, which is created by the van der Waals forces between adjacent phenyl rings on polystyrenes, breaks up and reforms within this temperature range.^{5c} This is related to the motions of the chain segments and can be attributed, in part, to the rotation of phenyl rings. Our results are in favor of the latter speculation, since the dimer model compounds is obviously unable to form a helical structure and yet it shows quantitatively the same temperature dependence of UV extinction coefficient as the isotactic polymer. On the other hand, the temperature dependences of ϵ of the syn-

diotactic-rich polymer and the *d,l*-isomer exhibit no detectable discontinuity as shown in Figure 3 (in the figure the value of ϵ only at about 261 nm is plotted against temperature).

Effect of the Sequential Arrangement of Monomers

Preliminary UV absorption measurements were carried out to examine the dependence of extinction coefficient on the sequential arrangement of monomers. Three different model ST-MMA copolymers (SM-AL, SM-Block, and SM-50) with nearly equimolar composition and a mixture of radically prepared PMMA and S-PS were used as reference samples. SM-Block and a mixture of PMMA and S-PS show the same UV spectra as S-PS, whereas the spectra of SM-AL and SM-50 are different from that of S-PS and even from each other; the extinction coefficients become smaller in the order of SM-Block, SM-50, and SM-AL. In addition, SM-Block takes the maximum absorbance at about 261 nm, while SM-AL and SM-50 take at about 259 nm (see Table III). The difference in ϵ values of SM-Block and SM-AL is as much as 0.4×10^2 ($l \text{ mol}^{-1} \text{ cm}^{-1}$) at about 261 nm. This means that the largest hypochromic effect is found when the ST units are flanked by MMA units on both sides and it amounts to about 20% at 261 nm.

Figure 4 shows UV spectra of SM-series copolymer samples with different ST contents. We can see the variation of the spectrum with ST content; when ST content is small it is similar to that for SM-AL and approaches that

for SM-Block with increasing ST content. The values of extinction coefficients at the peak or shoulder positions are summarized in Table III. The extinction coefficients of random copolymer lie between those of block and alternating co-

Figure 4. UV absorption spectra of random ST-MMA copolymers with different styrene contents in tetrahydrofuran at 25°C. Values described on each spectrum are styrene content (mol%).

Table III. Wavelength λ and extinction coefficient ϵ at peak and shoulder positions of ST-MMA copolymer samples in tetrahydrofuran solution at 25°C

Sample	λ , nm				$\epsilon \times 10^{-2}$, $l \text{ mol}^{-1} \text{ cm}^{-1}$			
	λ_1	λ_2	λ_3	λ_4	ϵ_1	ϵ_2	ϵ_3	ϵ_4
SM-20	269.3	265	262.5	259.5	1.102	1.383	1.660	1.796
SM-30	269.3	265	262.5	259.5	1.159	1.441	1.765	1.859
SM-40	269.3	265	262.5	259.5	1.243	1.514	1.848	1.942
SM-50	269	265	262	259.5	1.326	1.566	1.921	1.979
SM-60	269	265	261.5	259.5	1.368	1.593	1.963	2.015
SM-70	269	265	261.5	259.5	1.410	1.613	1.974	2.036
SM-80	269	265	261.5	259.5	1.545	1.640	2.001	2.052
SM-90	269	265	261.5	259.5	1.587	1.665	2.071	2.022
S-PS	269	265	261.5	259.5	1.598	1.675	2.086	2.030
SM-AL	269.5	265.5	262	259	1.094	1.397	1.699	1.813
SM-Block	269	265	261.5	259	1.585	1.667	2.073	2.024

polymers. The values of the three extinction coefficients (ϵ_2 , ϵ_3 , and ϵ_4) of sample SM-20 are smaller than the corresponding values of the alternating copolymer. This is ascribed to the experimental error, since the ST content in SM-20 is too small to measure the extinction coefficients accurately.

The measured extinction coefficients of random SM-series copolymers, ϵ_{av} , can be approximately expressed in terms of the probabilities of the three possible triads each with a ST unit in the center:^{12b}

$$\epsilon_{av} = f_{SSS}\epsilon_{SSS} + f_{MSS}\epsilon_{MSS} + f_{MSM}\epsilon_{MSM} \quad (1)$$

Here, S and M represent styrene and methyl methacrylate units, respectively. The probability of finding each triad in a random copolymer may be computed from the run number, which may also be deduced on the basis of copolymerization kinetics.^{13,15} Within the framework of the above approximation the extinction coefficient of homopolystyrene may be identified with ϵ_{SSS} , and that of alternating copolymer with ϵ_{MSM} . Rearrangement of eq 1 yields

$$\Delta\epsilon = \epsilon_{av} - (f_{SSS}\epsilon_{SSS} + f_{MSM}\epsilon_{MSM}) = f_{MSS}\epsilon_{MSS} \quad (2)$$

Thus, $\Delta\epsilon$ for a given wavelength should be proportional to the triad probability f_{MSS} with the proportionality constant ϵ_{MSS} , if the triad approximation is valid. This proportionality is confirmed for the SM-series copolymers as revealed in Figure 5. The slopes give 1.440 and 2.030×10^2 [$l \text{ mol}^{-1} \text{ cm}^{-1}$] for ϵ_{MSS} at 269 and 259 nm, respectively. This, in turn, means that the measured extinction coefficient of a given random ST-MMA copolymer allows us to evaluate the run number of the sample, if the three ϵ values, ϵ_{SSS} , ϵ_{MSM} , and ϵ_{MSS} are known, as eq 1 shows.

Turning our attention to the problem in GPC and MCC fractionation, it is evident that the point-by-point composition of ST determined by UV detector will be always underestimated considerably, if the hypochromic effect is not taken correctly into account. In the case of copolymers with low compositional heterogeneity or in the case where the variation of point-by-point composition with elution volume is negligible, this effect may be corrected by knowing the percentage of hypochromicity of the whole

Figure 5. Plots of triad probability f_{MSS} against $\Delta\epsilon$ according to eq 2 for random ST-MMA copolymers (cf. Table III) at 269 nm (●) and 259 nm (○).

polymer sample. In the case where the variation of point-by-point composition with elution volume occurs, however, it is not easy to solve this problem precisely by some simple calculations, because it is impossible practically to know the run number at each elution volume. In practice, therefore, we would like to suggest that the UV calibration curve for determination of the point-by-point composition should not be made with homopolymer but with copolymer of a type similar to a sample under fractionation. In fact, Probst, *et al.*,¹⁶ have obtained good results for the fractionation of ST-butadiene radical copolymer samples containing 5 to 30% of ST.

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