Appendix

Some observations reported by Hamann et al.[9] call for the following suggestions. Hamann et al. investigated polymerization of styrene initiated by perchloric acid in carbon tetrachloride and found the reaction to be zero order in the monomer but its rate proportional to $[\mathrm{HClO_4}]_0$; viz.

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = \mathrm{const} \times [\mathrm{HClO_4}]_0$$

They rationalized these results by invoking again the formation of complexes between growing polymers, the acid, and monomer. However, an alternative explanation is plausible.

Participation of two or more species in ionic polymerizations are well-known and documented.[7] Consider two interchangeable polymeric species, P_1^* and P_2^*, participating in a polymerization

$$P_1^* \underset{k_b}{\overset{k_f}{\rightleftarrows}} P_2^*$$

In most systems monomer addition converts an n-meric species of one kind into an $(n + 1)$-meric of the same kind; viz.

$$P_1^* \ (n\text{-mer}) + \mathrm{M} \xrightarrow{k_1} P_1^* \ ((n+1)\text{-mer})$$

$$P_2^* \ (n\text{-mer}) + \mathrm{M} \xrightarrow{k_2} P_2^* \ ((n+1)\text{-mer})$$

However, reactions of the type

$$P_1^* \ (n\text{-mer}) + \mathrm{M} \xrightarrow{k_{12}} P_2^* \ ((n+1)\text{-mer})$$

and

$$P_2^* \ (n\text{-mer}) + \mathrm{M} \xrightarrow{k_{21}} P_1^* \ ((n+1)\text{-mer})$$

are also feasible.[8] Let us assume that a system is governed by the following rate constants:

$$k_{12} \gg k_1, \qquad k_2 = 0, \qquad k_f \ll k_{12}[\mathrm{M}]$$

i.e., the monomer-induced conversion of P_1^* into P_2^* is faster than its propagation or its collapse into P_2^*, whereas P_2^* neither propagates nor is converted into P_1^* by the monomer, although a spontaneous conversion of P_2^* into P_1^* does take place. These relations do not violate the principle of microscopic balancing provided depropagation of any kind is sufficiently slow to be neglected. Under those conditions the rate of polymerization is

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_b[P_2^*] \approx k_b[\text{polymers}]$$

when $k_f/k_b \gg 1$. Such a polymerization is therefore zero order in monomer and first order in growing polymers, i.e., in $[\mathrm{HClO_4}]_0$.

This mechanism accounts for Hamann's findings without invoking the improbable complexes. It is premature to specify the nature of the species P_1^* and P_2^* proposed here. Tentatively one may consider P_2^*, which forms the bulk of the polymers, as a dormant, virtually inactive ester whereas P_1^* is its ion pair, which collapses into an ester on addition of the monomer.

Registry No. $\mathrm{HClO_4}$, 7601-90-3; styrene, 100-42-5.

References and Notes

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(9) S. D. Hamman et al., *J. Macromol. Sci., Chem.*, **A6**, 771 (1972).
(10) The peculiarity of the graphs giving log [HA] as a function of time is discussed in the next section.
(11) The reverse of reaction c yielding the indan derivative may be neglected. Such a derivative is assumed to be stable and should not generate the ester.
(12) K. Matyjaszewski et al.; *Acta Polym.*, **35**, 14 (1984).

Ultraviolet Analysis of Benzoyl Peroxide Initiated Styrene Polymerizations and Copolymerizations. 1

Luis H. Garcia Rubio,* N. Ro, and R. D. Patel

Xerox Research Centre of Canada, 2660 Speakman Drive,
Mississauga, Ontario, L5K 2L1 Canada. *Received June 24, 1983*

ABSTRACT: Ultraviolet spectroscopic quantification of the end groups resulting from the decomposition of benzoyl peroxide (BPO) during the initiation of styrene polymerizations and the application of such analysis to polymerization kinetics and to the development of polymer characterization techniques are reported. As an additional example of the application of ultraviolet spectroscopy to polymer analysis, the results obtained on commercial samples of poly(n-butyl methacrylate) and poly(isobutyl methacrylate) are also presented and discussed.

Introduction

The ultraviolet analysis of styrene-containing copolymers has been, in recent years, the subject of controversy. Hypochromic effects, band shifts, etc. have been attributed to characteristics of the microstructure of the polymer molecules and to conformation effects induced by both the polymer microstructure and the thermodynamic properties of the solvents used.[1-3] The nonideal absorption behavior observed appears mainly through deviations from the line typical of single chromophores. Correlation of these deviations with microstructure characteristics such as the length of the styrene sequences has been reported and used in conjunction with size exclusion chromatography for the characterization of styrene copolymers.[2,3,5] It has been shown, however, that within the limits of experimental error, the laws of linearity and ad-

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* Current address: Department of Chemical and Mechanical Engineering, College of Engineering, University of South Florida, Tampa, FL 33620.

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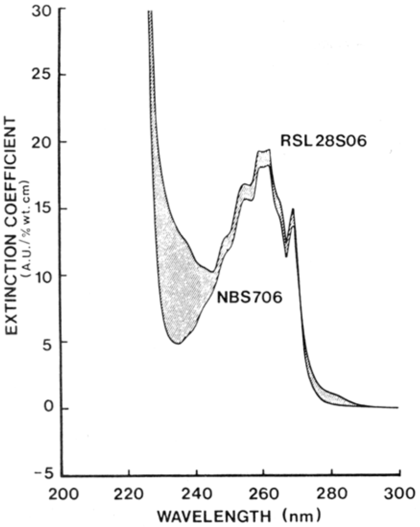


Figure 1. Difference between the spectra of a low-conversion thermally polymerized polystyrene (NBS-706) and a polystyrene synthesized with benzoyl peroxide.

ditivity of absorbances appear to be valid for a variety of styrene copolymers over the range of compositions reported.[4] The deviations from the absorption lines typical of single chromophores and the demonstration of the validity of the Beer–Lambert law over a composition range suggest that the identification of all the chromophores present in the polymer molecules has not been complete. Of particular importance is the presence of small concentrations of initiator fragments containing strong chromophores such as the benzoate groups resulting from the decomposition of benzoyl peroxide, which is a widely used initiator in the synthesis of homopolymers and copolymers. The presence of the initiator fragments can significantly alter the UV spectra (Figure 1) and, thus, affect both the interpretation and the quantification of the spectral data. This paper reports on the ultraviolet spectroscopic quantification of the end groups resulting from the decomposition of benzoyl peroxide (BPO) during the initiation of styrene polymerizations and on the application of such analysis to polymerization kinetics and to the development of polymer characterization techniques. As an additional example of the application of ultraviolet spectroscopy to polymer analysis, the results obtained on commercial samples of poly(*n*-butyl methacrylate) and poly(isobutyl methacrylate) are also presented and discussed.

Literature Review

Benzoyl peroxide is one of the most common free radical initiators; therefore, there is a large body of literature concerning its chemistry and decomposition reactions.[7,13] There is good consensus in the literature that BPO decomposes primarily into two active species by means of three decomposition reactions:

Primary Decomposition

$$\text{Ph–CO–O–O–CO–Ph} \rightarrow 2\text{Ph–CO–O}\cdot \tag{I}$$

Secondary Decomposition

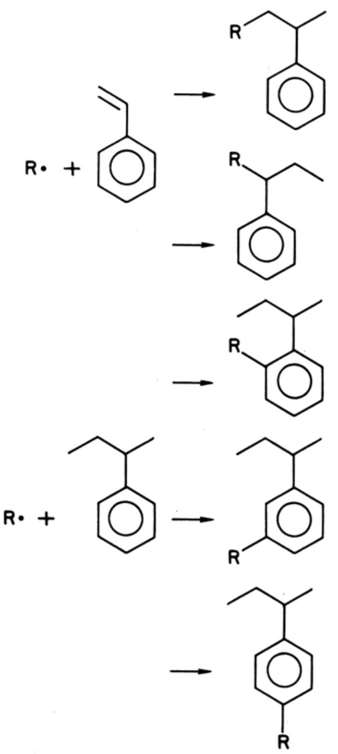
$$\text{Ph–CO–O}\cdot \rightarrow \text{Ph}\cdot + \text{CO}_2 \tag{II}$$

Induced Decomposition

$$\text{Ph–CO–O–O–CO–Ph} + \text{R}\cdot \rightarrow \text{Ph–CO–O}\cdot + \text{Ph–CO–OR} \tag{III}$$

The active species, benzoyloxy and phenyl radicals, are considered to be responsible for the initiation of the polymer chains, as well as for the formation of a wide variety of byproducts.[12,13] Thus, the presence of biphenyl, benzoic acid, and phenyl benzoate byproducts has been explained on the basis of reactions of the free radicals resulting from the decomposition of BPO.[12] The rate at which polymer chains are initiated has been found to depend both on the rate at which active species are generated and on the rate at which competing reactions take place. The type and frequency of the reactions that compete with the initiation of polymer chains are known to be a function of the temperature[8] and the nature of the reaction medium.[7,8,12,13] The BPO fragments attached to the polymer molecules as end groups can be expected to be products of the monomer and the benzoyloxy and phenyl radicals. The quantitative analysis of such groups, however, is not trivial, particularly in the case of styrene polymerizations, where recent studies[11-14] have shown that a large variety of products may result from the reactions of phenyl and benzoyloxy radicals with styrene molecules (Table I). Infrared spectroscopy, ^{14}C labeling, radical trapping agents, and ^{13}C-enriched benzoyl peroxide have been used to quantify the number of BPO fragments per polymer molecule obtained under a variety of polymerization conditions. In one of the early studies Pfann, Williams, and Mark[9] used infrared spectroscopy to investigate the presence of carbonyl groups in polystyrene initiated with BPO. Their studies indicate that the number of initiator fragments present in the polymer molecules is larger than the expected theoretical value based on two fragments per molecule, thus suggesting that the initiator radicals, particularly those formed during the later stages of the polymerization, react and become attached to previously formed polymer molecules. Bevington and Brooks[27] investigated the decomposition of BPO using polystyrenes synthesized at 60 °C with three types of ^{14}C-labeled benzoyl peroxides (i.e., uniformly, ring, and carbonyl labeled). By following the concentration of the initiator fragments after hydrolysis, these authors established the presence and estimated the concentration of both benzoyloxy and phenyl

Table I
End Groups Resulting from Benzoyl Peroxide Initiation of Styrene Polymerizations[11-14]



end groups. More recently, Berger, Deb, and Meyerhoff[11] reviewed the work done up to 1977 and investigated the reactions of BPO during styrene polymerizations using ^{14}C-labeled benzoyl peroxide in the temperature range 30–80 °C. These authors found that after hydrolysis of the ester end groups (i.e., benzoates) some ^{14}C activity remained in the polymer. The presence of this activity was explained on the basis of a transfer to initiator reaction with H exchange which resulted in a tertiary initiation step. In addition, Berger et al. estimated groups of rate constants for the decomposition reactions (eq I–III) and their concomitant monomer initiation and primary radical termination reactions. By using an efficient radical trapping agent (2,2,6,6-tetramethylpiperidine-1-oxyl), Moad, Rizzardo, and Solomon[13] have been able to examine the selectivity of the reaction of benzoyloxy radicals and styrene monomer at 60 °C. Because the reactions between the radicals and the radical trapping agent yield stable compounds, isolation and identification of the structure of the radicals formed have been possible (Table I). More recently, the same authors completed their investigation by quantifying the concentration of the initiator fragments using ^{13}C NMR and ^{13}C-enriched benzoyl peroxide on polystyrenes produced at 60 °C.

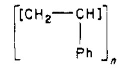
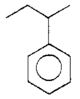
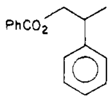
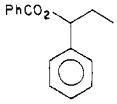
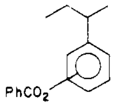
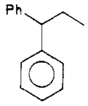
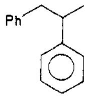
The structures shown in Table I constitute the end groups identified to date in polystyrene molecules initiated with BPO.[11-14] The formation and reactions of these end groups have also been used to explain some features of the initiation mechanism and the adverse thermal properties found in polystyrenes produced with BPO.[13,14] Therefore, they were used as guidelines for the selection of model compounds that enabled the quantification of the UV spectra of polymers containing BPO fragments.

Experimental Methods

Polystyrenes containing BPO fragments were synthesized via suspension polymerization in a 300-cm^3 Paar reactor at 90 °C. The reactor was heated by an electric mantle connected to the power supply through a variable transformer to maintain the temperature within 1 °C. The charge to the reactor consisted of a mixture of 120 cm^3 of deionized water and suspending agents, 60 g of styrene (Eastman Kodak), and 2.5% by weight benzoyl peroxide (J. T. Baker) on styrene monomer. The reaction was stopped at the desired interval by cooling the total mixture and filtering and washing the solid product repeatedly to eliminate the suspending agent. The polymer was then dissolved in spectral-grade tetrahydrofuran (Burdick and Jackson) and precipitated twice from absolute methanol. The conversions were determined gravimetrically. The molecular weights were determined by size exclusion chromatography in THF at room temperature. Five high-resolution Waters Scientific Ultrastyragel columns (100, 500, 10^3, 10^5, and 10^6 Å) were used for the analysis. The detection system consisted of a Waters 403 differential refractometer and a Chromatix LALLS photometer. The reproducibility in the estimation of the molecular weight averages was better than 2%.

The UV spectra of the polymers and model compounds in THF and a 1-cm path length cell were determined in a Hewlett-Packard diode array 8450 UV/Vis spectrophotometer at room temperature. Up to seven concentrations plus replicates were used in order to obtain good estimates of the extinction coefficients as well as good estimates of the measurement errors.[15] Special care was taken to ensure that the measurements were always within the linear range of the instrument. The raw data were transferred to a Data General S-230 Eclipse computer for processing. The solvent background and base line corrected spectra were used for the estimation of the compositions. The model compounds used are summarized in Table II.

Table II
Model Compounds

model compound	formula	mol wt	end or backbone group
polystyrene NBS-706	 $[\mathrm{CH_2{-}CH(Ph)}]_n$	$\bar{M}_w$ = 257 800, $\bar{M}_n$ = 136 500	
ethyl benzoate	$PhCO_2C_2H_5$	150.18	
benzyl benzoate	$PhCO_2CH_2Ph$	212.25	
phenyl benzoate	$PhCO_2Ph$	198.22	
diphenylmethane	$PhCH_2Ph$	168.24	
bibenzyl (1,2-diphenylethane)	$PhCH_2Ch_2Ph$	168.24	

Estimation of the Background Compositions

In order to identify and quantify the concentration of the groups present in the polymer molecules, the standard assumptions of linearity of absorption with respect to concentration and additivity of the individual spectra of the components have been used;[15] i.e.

$$A_j = \sum_{n=1}^{N} \epsilon_{nj} p_n I C \tag{1}$$

The linear behavior of the absorption with respect to concentration was statistically verified for all the substances used. The estimation of the extinction coefficients and compositions was done on a weight basis in order to minimize the propagation of experimental error.[15] The extinction coefficients of the model compounds are shown in Appendix I and the transformation to weight basis is described in Appendix II. (Appendices I and II are available as supplementary material.)

Several multivariate procedures have been proposed for the identification of components in mixtures, depending on how much is known about the mixtures and what has to be estimated from them.[17] In this case, because pure components are being used as the background models and the number of species likely to be present is relatively small (Table I), the simplest approach is to select those components that best predict the spectra of the unknown mixtures, i.e., to statistically eliminate those components that, within the limits of experimental error for the sample and for the background, cannot reduce the residual sum of squares between the measured and the calculated spectra.[15] The calculated spectra are obtained from eq 1 applied to all the concentrations over all the measured wavelengths. The objective function used in the minimization process is given by[15,17]

$$\min = \sum_i \sum_j \phi_{ij}^2 / \sigma_{ij}^2 \tag{2}$$

where

$$\phi_{ij} = A_{ij} - \sum_{n}^{N} \epsilon_{nj} p_n I C_i$$

$$\sigma_{ij}^2 = \mathrm{var}\,(A_{ij}) + \sum_{n}^{N} [IC_i p_n]^2 \,\mathrm{var}\,(\epsilon_{nj}) + [\sum_{n}^{N} I p_n \epsilon_{nj}]^2 \,\mathrm{var}\,(C_i)$$

Table III
BPO/Suspension-Polymerized Polystyrenes

sample	time, min	% conv	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$(g_{\text{initiator}}/g_{\text{polymer}}) \times 100$					% contribution		end groups/molecule
					a	b	c	$PhCO_2$	$PhCO_2Ph$	$PhCO_2$	$PhCO_2Ph$	
PS01	7	7.13	29.50	15.09	0.803	1.605	1.564	1.558	0.0054	99.65	0.35	1.95
PS02	20	26.34	30.58	15.91	0.761	1.523	1.580	1.566	0.0135	99.15	0.85	2.07
PS03	36	57.47	32.28	16.46	0.736	1.471	1.501	1.457	0.0443	97.05	2.95	2.04
PS04	60	72.97	35.03	17.86	0.678	1.356	1.4820	1.4156	0.0664	95.52	4.48	2.09
PS05	90	79.04	37.76	18.88	0.642	1.283	1.395	1.317	0.0777	94.43	5.57	2.17
PS06	120	85.74	41.78	19.82	0.611	1.222	1.336	1.246	0.0903	93.24	6.76	2.19
PS07	155	88.84	43.53	19.45	0.623	1.245	1.380	1.293	0.0870	93.70	6.30	2.22
PS08	240	91.59	46.65	21.56	0.564	1.129	1.357	1.253	0.1039	92.35	7.65	2.40

[a] Calculated assuming 1 end group/molecule. [b] Calculated assuming 2 end groups/molecule. [c] Calculated from UV measurements.

Alternatively, the differences between the measured (ϵ_j^0) and calculated extinction coefficients can also be used in the objective function. For this case, eq 2 becomes

$$\min = \sum_{j}^{\lambda}[(\epsilon_j^0 - \sum_{n}^{N}\epsilon_{nj}p_n)^2/\text{var}\ (\epsilon_{nj}) + \sum_{n}^{N}p_n^2\ \text{var}\ (\epsilon_{nj})] \quad (3)$$

where the variances of the extinction coefficients are estimated from the absorption measurements.[15]

The solution to the nonlinear equations (2) and (3) for the identified number of components yields the composition estimates.

The wavelengths for the analysis were selected on the basis of the variances obtained for both the unknown samples and the model compounds. It was observed that for most polymer samples the variance of the measurements increased sharply for absorbances measured below 230 nm. The reason for the increase in variance is the operation of the instrument in the region where the absorption is no longer linear. Therefore, in order to obtain, reproducible concentration measurements with high signal-to-noise ratio and, at the same time, account for most of the spectral features, the analysis was limited to the range 230–300 nm.

Results and Discussion

1. Styrene Homopolymers. The composition results obtained from the application of eq 2 or 3 depend on the selection of the model molecules used for the analysis. The low molecular weight model molecules can be obtained in high levels of purity and do not represent major problems. However, the selection of the model for the main component, polystyrene, is more difficult since the microstructure of the polystyrene molecules is known to affect the UV absorption spectrum.[2] The National Bureau of Standards polystyrene NBS-706 was selected as a model molecule for the following reasons: (a) The synthesis conditions (140 °C, thermal initiation, and 37% conversion) yield an essentially linear polymer. (b) The number-average molecular weight is sufficiently large to allow a good approximation in the estimation of the end groups resulting from the initiation using BPO. (c) High concentrations of double bonds conjugated with the phenyl ring that would result from the termination by a disproportionation mechanism could not be detected in the region around 280 nm (see Figure 1 and Appendix I). (d) No abnormalities in the UV spectrum are evident from comparisons with other published spectra. (See ref 1, 2, 5, and 25.) (e) NBS-706 is a standard material readily available and can be used for the normalization of the results between different laboratories.

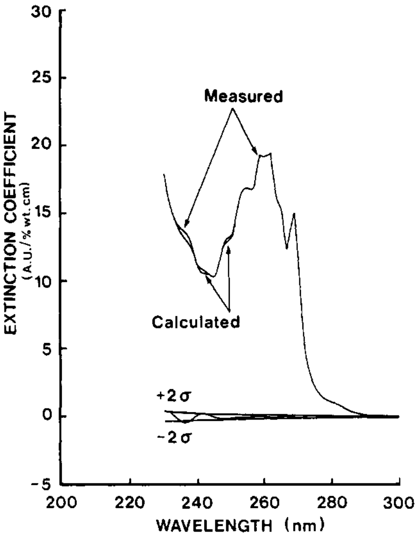


Figure 2. Comparison between measured and calculated spectra for polystyrene sample PS01. The 95% confidence interval (±2σ) on the measurements is also indicated.

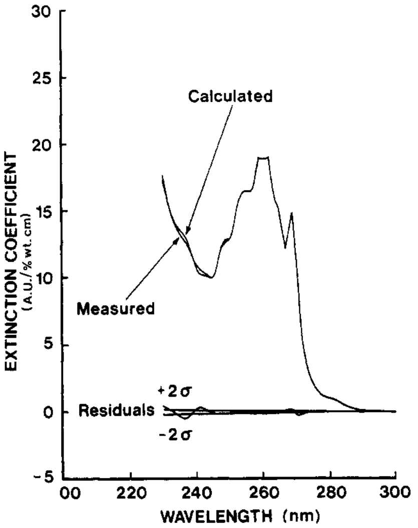
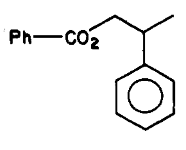
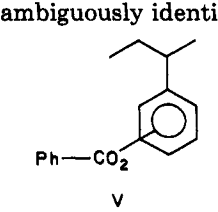


Figure 3. Comparison between measured and calculated spectra for polystyrene sample PS06. The 95% confidence interval (±2σ) on the measurements is also indicated.

Application of eq 3 together with the model compounds shown in Table II to polystyrenes synthesized with BPO at 90 °C (Table III) resulted in only two main groups of initiator fragments being unambiguously identified:



IV



V

The use of the corresponding model compounds for these

Table IV
Polystyrenes Produced at 60 °C (Data from Ref 14)

sample	reacn time, min	% conv	$[I]_0$, M	$\bar{M}_n \times 10^{-3}$	$(g_{BPO}/g_{polymer}) \times 100$ *a*	*b*	*c*	*d*
A	295	8	0.01	170	0.010	0.010	0.014	0.011
B	150	8	0.04	81	0.025	0.023	0.030	0.024
C	92	8	0.10	45	0.404	0.347	0.538	0.431
D	470	30	0.10	44	0.440	0.361	0.551	0.440
E	960	80	0.10	46	0.606	0.376	0.527	0.421

[a] Total concentration of end groups from NMR. [b] Concentration of benzoates resulting from vinyl double-bond additions. [c] Concentration of end groups calculated from $\bar{M}_n$ and 2 end groups/molecule. [d] Concentration of end groups calculated from *n* and 1.6 end groups/molecule.

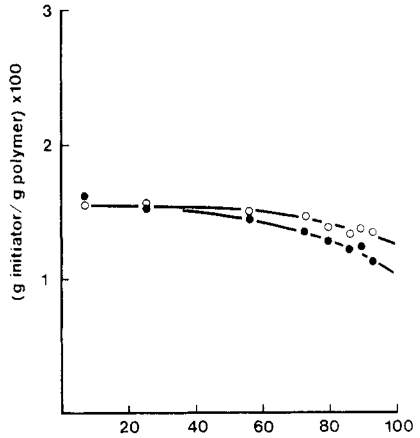


Figure 4. Comparison of the UV-measured initiator fragments (○) with calculated concentrations based on the molecular weight data and the assumption of 2 end groups/molecule (●).

two ester groups (Table II) always gave good recoveries of the measured spectra, as shown in Figures 2 and 3. The precision of the composition estimates (i.e., 2σ level in percent weight or $(g_{initiator}/g_{polymer}) \times 100$ based on the pooled variance for replicate measurements is as follows: PS, ±0.2, $PhCO_2$, ±0.02, $PhCO_2Ph$, ±0.01. The identification of the above two benzoate groups as major components of the UV spectra is not surprising in view of the available experimental data,[11-14] which suggests that the contribution of the secondary decomposition products of BPO to the total initiation rate is less than 1% at 90 °C. Comparison of the measured concentration of BPO fragments with the calculated concentrations, based on the molecular weight data and termination by combination, agrees with previous observations,[9,14] indicating that, up to intermediate conversions, the concentration of initiator fragments follows the molecular weight trend (Figure 4). The proportion of aromatic benzoates estimated from the UV measurements increases with increasing conversion (Figure 5), suggesting that at 90 °C a significant fraction of the initiator fragments react with the polymer to yield polystyrene with three or more initiator fragments. A similar observation has been made by Moad et al.[14] for polystyrenes produced at 60 °C. Comparison of the concentration of benzoate groups attached to the backbone of the polymer chain (i.e., those resulting from addition to the vinyl double bond) to the concentration of end groups calculated from molecular weight data (columns 6 and 8 in Table III) supports the hypothesis that the aromatic benzoates do not result from an initiation reaction but rather are the product of a grafting reaction, in which case the concentration of aromatic benzoates should increase with conversion. As expected, the fraction of aromatic benzoates increases with increasing conversion (Figure 5). This observation is consistent with the data available at 60 °C,[14] particularly if the expected number of end groups per molecule at 60 °C[21] (approximately 1.6) is used for the calculation (Table IV and Figure (6)).

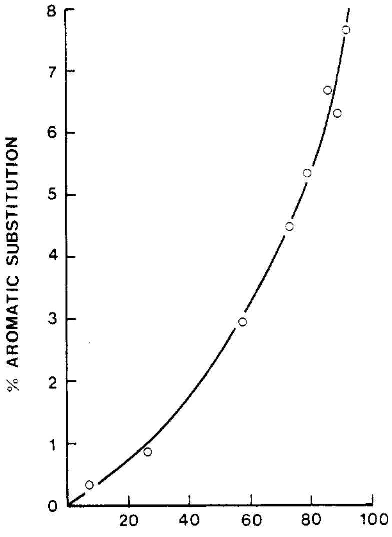


Figure 5. Comparison of the percentage of aromatic substitution as a function of conversion for BPO-initiated styrene polymerizations at 90 °C.

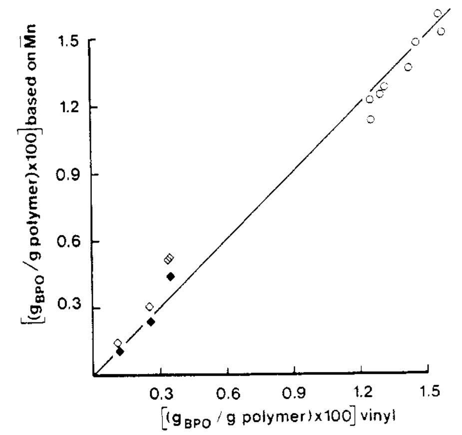


Figure 6. Comparison of the concentration of end groups calculated from molecular weight data and UV measurements of the benzoate groups resulting from addition to the vinyl double bond: (○) 90 °C; (◇) 60 °C with 2 end groups/molecule; (◆) 60 °C with 1.6 end groups/molecule. Data at 60 °C from ref 14.

An important result for the understanding of polymerization kinetics, which stems directly from the analysis of the initiator fragments, is the estimation of the initiator efficiencies. Traditionally, the rate of polymerization is expressed as

$$R_p = k_p[M]\left(\frac{R_i}{k_t}\right)^{1/2} \tag{4}$$

where k_p, k_t, [M], and R_i have their usual meaning of propagation rate constant, termination rate constant, monomer concentration, and rate of initiation. The rate

Table V
Commercial Poly(butyl methacrylates)

	$\bar{M}_n \times 10^{-3}$ [a]	$\bar{M}_w \times 10^{-3}$ [a]	$PhCO_2$, wt %	residual BPO, wt %	end groups/molecule[b]	$\bar{M}_n \times 10^{-3}$ [c]
PnBMa	73.5	320	0.420	0.962	2.58	57.0
PiBMA	140	300	0.233	0.860	2.70	104

[a] Quoted by the manufacturer. [b] Calculated based on the manufacturer's molecular weight. [c] Calculated assuming 2 end groups/molecule.

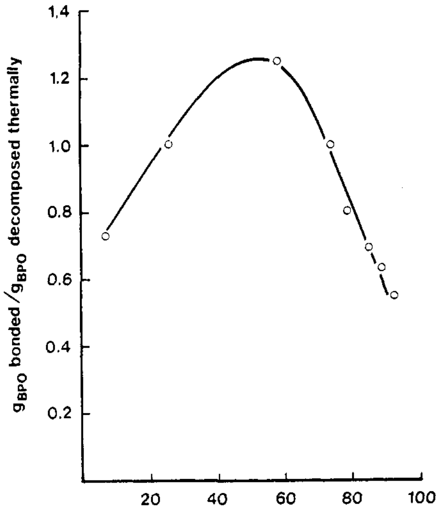


Figure 7. Initiator selectivity along the conversion trajectory, expressed as the ratio of the grams of initiator bonded to the polymer to grams of initiator decomposed by first-order thermal decomposition.

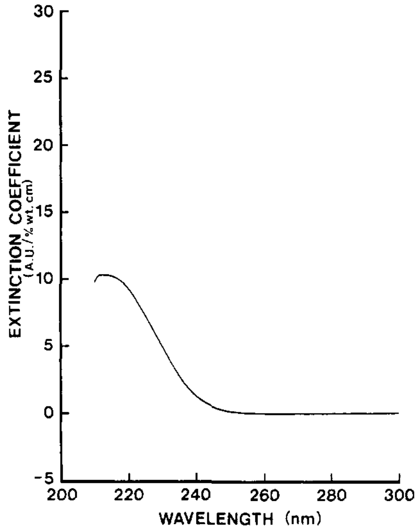


Figure 8. Extinction coefficients for poly(butyl methacrylates) obtained from the extinction coefficient of poly(methyl methacrylate).

of initiation for a first-order decomposition and under the stationary-state hypothesis is given by

$$R_i = 2fk_d[I]_0 \exp(-k_d t) \qquad (5)$$

where f is an empirical efficiency factor with values between 0 and 1. In other words, f represents the selectivity of the initiator toward initiation reactions. It is normally recommended that, although f may vary with reaction temperature and conversion, it should be taken as a constant for practical calculations.[11,24] Therefore, if the above assumption is valid, the measured concentration of benzoate fragments divided by the cumulative amount of initiator that has been thermally decomposed (i.e., by first-order decomposition) should yield a horizontal line throughout most of the conversion history. As shown in Figure 7, this does not appear to be the case; a continuous increase is observed up to values greater than 1 at intermediate conversions followed by a decrease toward the end of the polymerization, suggesting that the decomposition of the initiator has an important effect on both the rate of polymerization and the resulting polymer properties. The rate constant for the thermal decomposition of BPO was taken as[11] $\ln k_d = 36.68 - 137.48/RT$ kJ/(g mol). It is clear that thermal decomposition on its own cannot explain the behavior shown in Figure 7, since more radical fragments are being incorporated onto the polymer chain than are being generated by thermal decomposition. Possible mechanisms that could enhance the production of initiator fragments include transfer reactions and the induced decomposition of the initiator. The latter is conceptually attractive, particularly at high initiator levels, where the induced decomposition of the initiator by other initiator fragments and polymer radicals would generate an "autocatalytic" effect. However, at this point, there are insufficient experimental data to allow the quantitative testing of the possible reaction paths. A detailed discussion of the implications of these results for the formulation of kinetic models will be published shortly.[19]

It is evident from the results thus far presented that ultraviolet spectroscopy can yield consistent information on the type and concentration of the BPO fragments that either initiate or react with polystyrene molecules. The importance of these measurements for the understanding of the polymerization kinetics as well as the resulting polymer properties cannot be overemphasized.[14,22,23] Furthermore, assessment of the contribution of the initiator fragments to the total absorption of polymer and copolymer samples is critical for the calibration of spectrometers used in polymer characterization applications (size exclusion chromatography, light scattering, etc.) which are dependent on accurate composition estimates. As shown in Figure 1, if the contributions of the benzoate groups are neglected, the copolymer compositions estimated from the UV measurements will be biased by the amount corresponding to the wavelengths selected to monitor the composition.

2. Other Polymers. The spectroscopic analysis described for polystyrene can be readily extended to the analysis of other polymer systems. In order to demonstrate this, two commercial standards of poly(n-butyl methacrylate) (Aldrich, catalog no. 18, 153-6) and poly(isobutyl methacrylate) (Scientific Polymer Products) have been analyzed (Table V); in addition to the BPO model compounds, a model for the methacrylate moiety is required. A good approximation for the latter can be obtained from poly(methyl methacrylate) (Figure 8). The results obtained (Table V) indicate that, in addition to the methacrylate monomer units and the benzoate fragments, complete benzoyl peroxide molecules were present in both polymers. (Figures 9 and 10 show the comparison between the calculated and the measured spectra.) The presence of residual initiator was verified by purification of the polymers by dissolution in THF and precipitation in absolute methanol. If the molecular weights reported by the

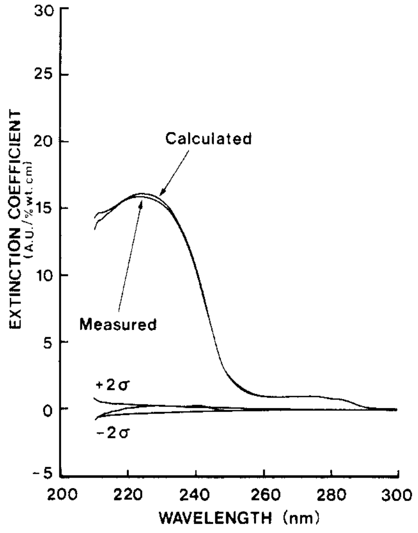


Figure 9. Comparison between the measured and calculated spectra for poly(n-butyl methacrylate).

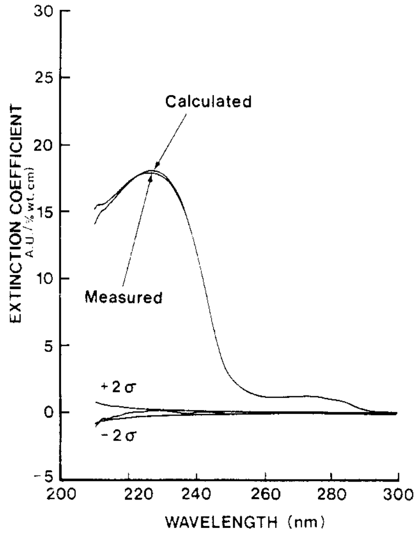


Figure 10. Comparison between the measured and calculated spectra for poly(isobutyl methacrylate).

manufacturer are assumed to be valid, then the calculated number of end groups per molecule indicates that these polymers may be branched. Alternatively, if it is assumed that there are only two end groups per molecule, the manufacturers' values for $\bar{M}_n$ appear to be off by approximately 22–25%. It is important to emphasize that for these polymers, as in the case of polystyrenes, incomplete characterization can lead to serious errors in both the interpretation and the quantification of UV results. For example, the poly(n-butyl methacrylate) standard analyzed here has been used extensively for the calibration of UV detectors used for the characterization of styrene–n-butyl methacrylate copolymers in liquid chromatography experiments.[25,26] The absorption band at 235 nm, which was selected for the analysis is formed by approximately 50% absorption due to the benzoate group and 50% due to the butyl methacrylate units. If no correction is applied to account for the presence of the benzoate groups, the result will be an overestimation of the styrene concentration.

Summary and Conclusions

The UV spectroscopic analysis of polystyrenes synthesized with benzoyl peroxide has been conducted by using model compounds for the BPO fragments attached to the polymer molecules. The results obtained indicate that UV spectroscopy can provide sufficient information for the quantification of the initiator fragments bound to the polymer molecules. The consistency of the values obtained for the concentration of the various species present in the polymer molecules has been verified against other measured known properties such as molecular weights or reported initiator decomposition rates. The UV-measured values have also been compared with available literature data obtained by other analytical techniques. The application of the same model compounds to the analysis of commercial poly(butyl methacrylate) standards suggests that the technique can be extended to a wide variety of materials. Two observations derived from the analysis done have important implications for the use of UV spectroscopy as a polymer characterization technique.

(i) The use of model compounds appears to be adequate for the identification and quantification of the chromophores present in the polymer molecules.

(ii) The laws of linearity (Beer–Lambert) and additivity of the chromophores appear to be valid provided all of the important chromophores have been identified. Therefore, the presence of initiator fragments should not be neglected based solely on their molar concentration.

The quantity and the quality of the information obtained from the UV analysis of polymer samples indicate that, although it does not yield as detailed structural information as, for example, NMR does, ultraviolet spectroscopy can, nevertheless, be a very powerful tool in the investigation of polymerization kinetics and for the characterization of polymers. In addition, it offers significant advantages in terms of its instrumentation and sensitivity.

(i) UV spectroscopy is sensitive enough for the detection of small quantities of material provided strong chromophores are present.

(ii) UV instrumentation is very common and can be easily adapted to plant and quality control operations.

(iii) Routine analysis of samples produced with standard materials can be easily conducted.

(iv) Combined with size exclusion chromatography, it can provide a detailed breakdown of polymer composition as a function of molecular size as well as provide the necessary information for the estimation of molecular weights when composition-sensitive methods such as viscometry or light scattering are being used.

In conclusion, a UV technique has been developed that enables the initiator-derived functionality in vinyl polymers to be readily determined when such functionality contains chromophores. The method of analysis has been demonstrated by evaluating the benzoate groups that are present in polystyrenes and commercial poly(butyl methacrylates) which have been synthesized with benzoyl peroxide as initiator. The simplicity of the UV analysis makes it amenable to chromatography experiments, from which detailed structural information can be obtained as functions of the molecular size. We are currently extending our work in this direction, with particular emphasis on the characterization of branched molecules, and will report on these in the near future.

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List of Symbols

A absorbance (AU)

C	polymer concentration (percent weight unless otherwise indicated)
f	initiator efficiency
g	grams
[I]	initiator concentration ((g mol)/L)
k	reaction rate constant
l	cell path length (cm)
M	molecular weight
[M]	monomer concentration
$\bar{M}_n$	number-average molecular weight
$\bar{M}_w$	weight-average molecular weight
N	number of species present in the solution
p	weight fraction
R_p	rate of polymerization
R_i	rate of initation
x	mole fraction
ϵ	extinction coefficient (AU)/[(% wt) cm] unless otherwise indicated
λ	wavelength (nm)

Subscripts

i	ith concentration
j	jth wavelength
M	molar
n	nth component
0	initial value
T	overall

Registry No. BPO, 94-36-0; polystyrene (homopolymer), 9003-53-6; poly(butyl methacrylate) (homopolymer), 9003-63-8; poly(isobutyl methacrylate) (homopolymer), 9011-15-8; ethyl benzoate, 93-89-0; benzyl benzoate, 120-51-4; phenyl benzoate, 93-99-2; diphenylmethane, 101-81-5; bibenzyl, 103-29-7; styrene, 100-42-5.

Supplementary Material Available: UV spectra of the model compounds (Appendix I) and Beer–Lambert law for weight-based measurements (14 pages). Ordering information is given on any current masthead page.

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Study of the Microstructure of Tetrahydrofuran–3-Methyltetrahydrofuran Copolymers: Computer Simulation of the Copolymerization Reaction

Julio Guzmán,* Leoncio Garrido, and Evaristo Riande

Instituto de Plásticos y Caucho, CSIC, Madrid 6, Spain. *Received October 17, 1983*

ABSTRACT: The cationic copolymerization of tetrahydrofuran (A) and 3-methyltetrahydrofuran (B) was studied at 0 °C with acetylhexafluoroantimonate as initiator. The values of the apparent reactivity ratios, calculated by the Kelen–Tüdos method, were $r_A^{ap} = 0.78 \pm 0.06$ and $r_B^{ap} = 0.15 \pm 0.05$. Values of both the composition and the dyad probabilities were obtained by ^{1}H NMR and ^{13}C NMR spectroscopy, respectively. The microstructure of the copolymers determined from the apparent reactivity ratios differs from that obtained by ^{13}C NMR spectroscopy, indicating that the THF–MTHF system does not obey the classical kinetic scheme in which only four propagation constants are considered. Monte Carlo computer simulations of the copolymerization with complete reversibility were made. Good agreement between the simulated values of both the composition and dyad probabilities with the experimental ones was obtained for the following values of the cross-propagation and depropagation rate constants: $k_{ab} = 6 \times 10^{-3}$, $k_{ba} = 3.5 \times 10^{-3}$ (both in L mol^{-1} s^{-1}) and $k_{-ab} = 5 \times 10^{-3}$, $k_{-ba} = 80 \times 10^{-3}$ (both in s^{-1}).

Introduction

The Mayo–Lewis equation has been traditionally used to determine the reactivity ratios of copolymers in which depropagation reactions are absent. The possible use of irreversible copolymerization equations of this type for the description of reversible reactions was studied by O'Driscoll et al.[1,2] in the analysis of some copolymerization systems in which reversibility of the propagation reactions must