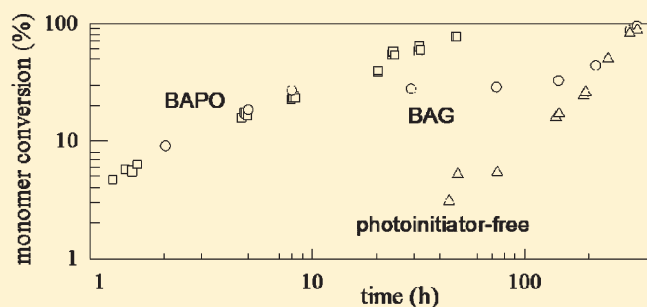


Photoinitiated Bulk and Emulsion Polymerization of Styrene — Evidence for Photo-Controlled Radical Polymerization

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ABSTRACT: A comparative experimental study of bulk and emulsion polymerization of styrene with bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) or bis(4-methoxybenzoyl)diethylgermanium (BAG) as photoinitiator or photoinitiator-free reveals astonishing similarities and anticipated differences. Expectedly, both the rate of polymerization and the molecular weight is higher for emulsion than for bulk polymerization. Unexpectedly, the polymerizations continue even if the photoinitiators have been used up and moreover, the average molecular weights increases with monomer conversion. Consideration of all experimental data gives rise to the proposal that the common feature of these polymerizations is photo electron transfer between styrene monomer and a repeating unit in the polystyrene chain.



INTRODUCTION

In recent years, photoinitiated polymerizations have received revitalized interest due to their wide range applications in coatings, adhesives, inks, printing plates, and optical waveguides.¹ In contrast to the thermal counterpart, photo polymerizations can be conducted at room temperature or below which is advantageous in many applications. There is no restriction regarding the kind of polymerization as bulk, solution and heterophase polymerization system can be carried out. Photopolymerizations may be initiated via cationic² or free radical³ mechanism. Although cationic photo polymerizations have received interest in recent years, the free radical route is more advanced mainly due to the availability of a wider range of monomers and photoinitiators acting at different wavelengths. Numerous cleavage and H-abstraction type photoinitiators with different absorbance characteristics, quantum efficiencies and solubilities are available.⁴ For many applications particularly those involving styrene monomers cleavage type photoinitiators are more preferred because of their low quenching rate of excited triplet states of the photoinitiators by styrene monomer.⁵ Among cleavage type photoinitiators, acyl phosphine oxides⁶ and acyl germanium⁷ are efficient photoinitiators with absorption characteristics that compare favorably with benzoin derivatives. Moreover, they are thermally stable and photochemically generated radicals exhibit high reactivity arising from the high electron density and favorable steric conditions particularly in the case of acylphosphine oxides. The absorptions in the visible spectral range and molar extinction coefficients of these photoinitiators were raised with the introduction of a second acyl group.⁸

The photoinitiators used in this study and their photoinduced sequential decompositions are shown in Scheme 1.

Emulsion polymerization is a widely used industrial process for manufacturing a variety of polymer colloids and particles for numerous applications such as coatings, adhesives, binders, and paints. Most of the studies on emulsion polymerization processes primarily concern thermally initiated polymerization and corresponding photopolymerizations have been scarcely investigated.⁹ The reported examples mostly involve micro emulsions¹⁰ in which high surfactant concentrations are used. In the photochemical conventional photoinitiated emulsion polymerizations usually water-soluble photoinitiators are used.¹¹

The aim of this work is to evaluate the photoinitiating behavior of two representative cleavage type bisacyl photoinitiators, namely bisacylphosphine oxide (BAPO) (bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide) and bisacylgermanium (BAG) (bis(4-methoxybenzoyl)diethylgermanium) (cf. Scheme 1).

The approach is to utilize photoinitiators with bisacyl functionality that upon irradiation with the UV or visible light undergo sequential photodecomposition. It is expected that such photoinitiators would have an influence on the conversion, molecular weight and size of the particles. Moreover, comparison experiments have been carried out in the absence of photoinitiators in order to get an idea about the importance of styrene self-photoinitiation in soda-lime silica glass vials with common fluorescent tube (light color 840, used frequently for indirect lighting in laboratories and other work rooms). Surprisingly, the experimental results reveal a kind of photocontrolled free radical

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Scheme 1. Photoinduced α -Cleavage of Bis(2,4,6-trimethylbenzoyl)phenylphosphine Oxide (BAPO, top) and Bis(4-methoxybenzoyl)diethylgermanium (BAG, bottom)

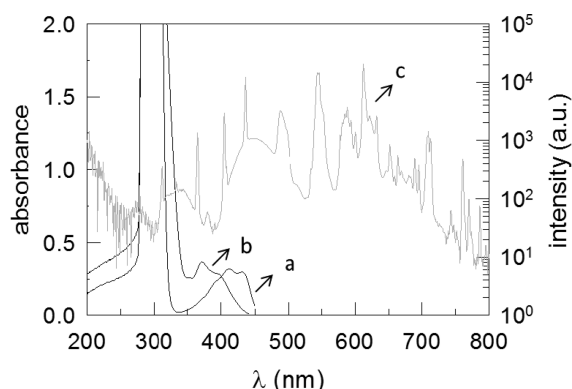
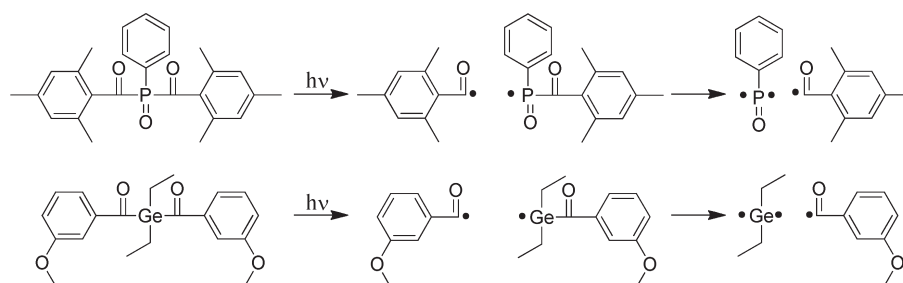


Figure 1. UV–vis absorption spectrum (left y-axis) of BAG (a) and BAPO (b) vapor as well as the fluorescence tube relative emitted light intensity spectrum (c) (right y-axis).

polymerization behavior in all investigated polymerizations. The obvious conclusion is that the mechanistic origin lies in an up until now unknown effect in the photochemistry of the styrene–polystyrene system.

EXPERIMENTAL SECTION

Materials. Styrene (99% purity, Sigma-Aldrich) was distilled under reduced pressure to remove inhibitors and stored in a refrigerator. Sodium dodecyl sulfate (SDS) ($\geq 99\%$ f.d. Elektrophorese ROTH), bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO or Irgacure 819) (Ciba Specialty Chemicals), bis(4-methoxybenzoyl)diethylgermanium (BAG) (a gift from Ivoclar Vivadent AG) and ethylbenzene (Merck) were used as received. The deionized water was taken from a Seral purification system (PURELAB Plus) with a conductivity of $0.06 \mu\text{S cm}^{-1}$.

Polymerization. All polymerizations were carried out at 25°C between two standard fluorescent tubes (Osram L 18 W, light color 840, lumilux, cool white, cf. spectral intensity distribution Figure 1) in 30 mL sample vials (neoLab) with a Teflon stirring bar at a stirring velocity of 400 rpm. The standard recipe for the emulsion polymerization was: 20 g of water, 4.5 g of styrene, 0.6 g of SDS and 0.048 mmol of initiator. For the bulk polymerization the same molar ratio of initiator per mass of styrene was used.

For investigating the photoinitiator decomposition and performing polymerizations the glass vials were placed in the middle between two fluorescence tubes (midpoint distance between one tube and the vial is 15 cm) on a magnetic agitation plate. The irradiance reaching the reaction mixture was estimated by an indirect measurement as described in.¹² Briefly, after placing the covered vials and allowing for thermal equilibration the cover was removed and the temperature increase

monitored. The irradiance (E) was calculated from the slope of the initial linear part of the temperature (T) – time (t) curve (dT/dt) according to $E = (c_{p,c} \times m_c + c_{p,g} \times m_g)/(A_v)(dT/dt)$. Taking into account the mass of the reaction vial ($m_g = 22.27$ g), the specific heat capacities of coffee black (assuming here that it corresponds to the value of water $c_{p,c} = 4.2 \text{ J g}^{-1}\text{K}^{-1}$) and glass ($c_{p,g} = 0.8 \text{ J g}^{-1}\text{K}^{-1}$), and the illuminated surface area ($A_v = 47.12 \text{ cm}^2$) an average irradiance of 0.5 mW/cm^2 was estimated in several repeats. This value is only about 1% of the averaged solar irradiance in Germany¹² and about 10% of the irradiation used in other styrene photopolymerizations.¹³

Characterization. The solids content (FG) was characterized with a HR 73 halogen moisture analyzer (Mettler Toledo, Giessen, Germany). The intensity-weighted average particle size (D_i) was measured by dynamic light scattering with NICOMP particle sizer (model 380 PSS, Santa Barbara, CA). Molecular weight distributions (MWD) were determined by size exclusion chromatography (SEC) on the basis of polystyrene standards (PSS; Germany). The SEC was run at 25°C in THF (flow rate 1 mL/min, 0.15 wt % polymer solutions) using a Thermo-Fischer-Scientific apparatus equipped with UV (UV-2000 operated at 260 nm) and RI (Shodex-RI-71) detectors. The column set consists of three 8×300 mm columns filled with PSS SDV with an average particle size $5 \mu\text{m}$ having pore sizes of 10^3 , 10^5 , and 10^6 \AA .

The intensity spectrum of the fluorescence tube was recorded with a photonic multichannel analyzer C10027 (Hamamatsu, Japan). The intensity spectrum of the fluorescence tube is shown in Figure 1 together with the absorption spectra of BAPO and BAG. In order to illustrate the absorption of the photoinitiators in the visible range of the spectrum (wavelength above 300 nm) their concentration was chosen quite high so that in the UV-range of the spectrum the absorption is truncated.

UV–vis absorption spectra were recorded with a UVIKON 931 spectrometer (Kontron Instruments, U.K.) in a wavelength range between 600 and 190 nm in quartz cuvettes with an optical path length of 2 mm. The extinction coefficients of the photoinitiators were determined in ethylbenzene and styrene at different concentration. Photoinitiator decomposition was studied with solution containing $9.6 \times 10^{-3} \text{ mol L}^{-1}$ photoinitiator also in these solvents. After given irradiation time, 200 μL of the solution were withdrawn and poured into 800 μL ethylbenzene for recording the UV–vis spectra. The decomposition rate coefficient of the initiators was calculated by means of the first-order kinetics where the slope of the linear regression line $\ln([I]_0/[I])$ vs time represents the rate coefficient ($[I]_0$ represent the concentration at $t = 0$, $[I]$ is the concentration at a given time).

¹H and ¹³C NMR measurements were carried out at room temperature using a Bruker DPX-400 spectrometer in CDCl_3 (Sigma-Aldrich).

RESULTS AND DISCUSSION

Absorption Characteristics and Photodecomposition Behavior. UV–vis absorption characteristics of the photoinitiators

such as the wavelength of maximum absorption (λ_{max}) and the molar extinction coefficient (ϵ) are summarized in Table 1.

Both photoinitiators show strong absorptions in the near UV and the visible region of the spectrum arising from $n-\pi^*$ transitions (cf. Figure 1). Several absorption maxima were attributed to the different angles of carbonyl groups to the central phosphonyl and dialkylgermyl groups. Notably, BAG absorbs more intensively in the visible region. It is known that, upon irradiation due to the presence of two carbonyl groups present in the structure, bisacyl photoinitiators undergo sequential decomposition^{8a,14} (Scheme 2).

It was recently demonstrated that block copolymers¹⁵ of structurally different monomers as well as polygermanium¹⁶ can be prepared by taking advantage of such decomposition behavior.

Table 1. Wavelength Maxima and Molar Extinction Coefficient of BAPO and BAG in Ethylbenzene

initiator	λ (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
BAPO	371	727
	396	919
BAG	412	830
	430	770

The data summarized in Figure 2 suggest that the photodecomposition of BAPO and BAG depends strongly on the solvent, either ethylbenzene or styrene. The decomposition rate constants summarized in Table 2 confirm this assumption.

Notably, the rate constant for the decomposition in the visible wavelength region are for BAG up to three times higher than for BAPO. Both initiators possess higher decomposition rate constant in ethylbenzene than in styrene. Obviously the radicals do not recombine to the starting material but generate different descendant products. The apparently slower decomposition of the photoinitiators in the monomer is somehow connected with the polymerization reaction. Benzoyl radicals react slower with styrene¹⁷ and hence, the growing and terminated polymer chains possess one and two photoactive chain ends, respectively. This chain ends exhibit absorptions in a similar wavelengths region. This behavior is particularly detectable with BAPO where prolonged irradiation results in the development of a new absorption band at 380 nm corresponding to the absorption of monoacylphosphine oxide.^{8a} The photochemical scission, initiation and coupling reactions may repeatedly occur during the photolysis and the chain ends can be photochemically activated at any stage of the polymerization. Thus, the process represents some characteristics of living systems and may be considered as

Scheme 2. Photopolymerization of Styrene with BAPO and Sequential Decomposition of Phosphine Oxide End Groups

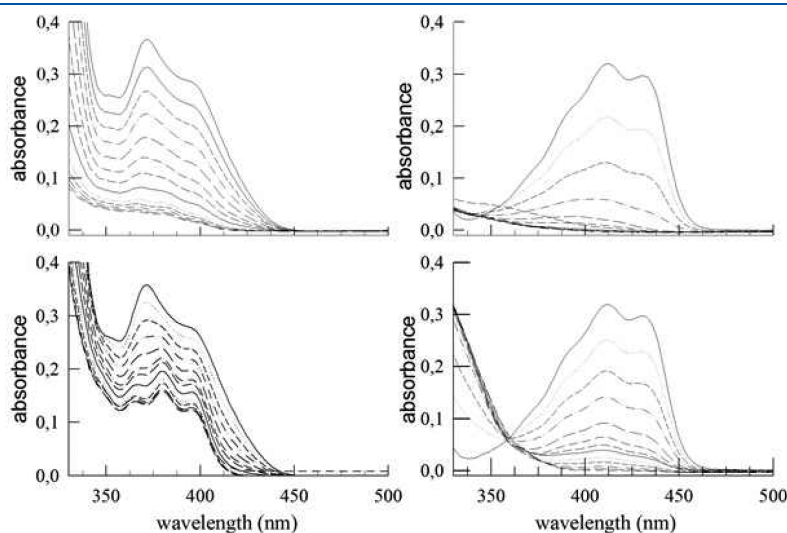
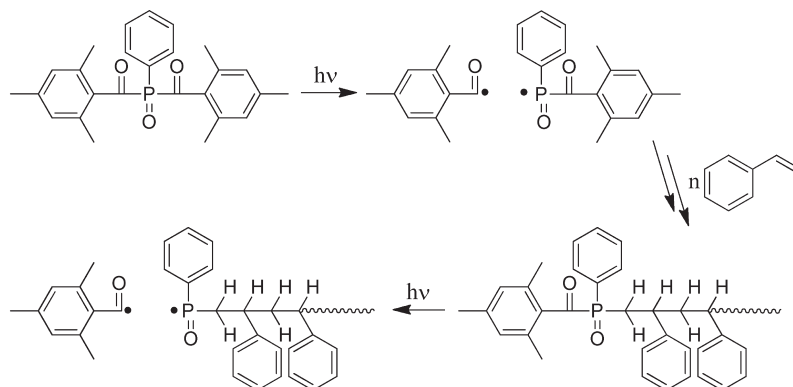


Figure 2. Photodecomposition behavior of BAPO (left) and BAG (right) in ethylbenzene (top) and styrene (bottom). Spectra were recorded every half an hour.

kind of phototriggered “quasi-living” polymerization. This issue will be further investigated in detail below.

Bulk Photopolymerization. In order to get more insight into the photoinitiation mechanism using bisacyl photoinitiators, it seemed appropriate to investigate photopolymerization of bulk styrene in detail. In Figure 3, time–conversion curves for the bulk photopolymerization of styrene using BAPO and BAG are plotted. For comparison, results of photoinitiated styrene polymerization (in the absence of photoinitiator) are also included.

It is seen from Figure 3 that with BAPO as photoinitiator, the polymerization is fastest with smoothly increasing conversion but slightly decreasing rate ($d(\text{conversion})/dt$) with time. The conversion of the photoinitiated styrene polymerization in the absence of photoinitiator also increases smoothly with time, however, with increasing rate. Interestingly, for BAG the conversion–time plot combines both behaviors. Initially the data points overlap with the BAPO curve and after about 25% of conversion the data follow the photoinitiator-free plot but are shifted parallel to higher conversion. This distinctly different behavior of the three systems can be attributed to two entirely different factors: (i) differences in the decomposition quantum yield (Φ_{dec}) and (ii) possibly a dead end polymerization scenario. It is reported^{8a} that the Φ_{dec} values for mono and bisacylphosphine oxides are almost identical (0.55 and 0.59, respectively). Completely different situation is encountered for the corresponding acyl–germanium photoinitiators. While the bisacyl-derivatives decompose with high quantum efficiency ($\Phi_{\text{dec}} = 0.85$) it is much lower for the monoacyl-germanium derivatives ($\Phi_{\text{dec}} = 0.40$).^{8a} Considering the chain ends are monoacyl germanium structures further generation of initiating

radicals is correspondingly decreased whereas it is almost unchanged for BAPO. Obviously, this effects the overall conversion. Besides the Φ_{dec} dead end polymerization may be responsible for the slow polymerization. In this case, the polymerization reaches a limiting conversion as a consequence of the depletion of the photoinitiator. For BAG and BAPO the concentration is ceased after 10 and 20 h, respectively. The overall polymerization time is much longer and hence, a so-called dead-end polymerization cannot be excluded in these cases. This possibility is more likely to occur in the case of BAG, as the photodecomposition is faster and primary radical concentration higher. Thus, the termination reaction between growing chains and primary radicals is more favorable. Then, the much slower decomposition of the chain ends gives rise to reduced polymerization rate. Very likely, both Φ_{dec} and dead-end polymerization contribute to the observed behavior. In addition, the similarity of the shape of the solids content–time curves for BAG and photoinitiator-free polymerization supports the conjecture that photochemical styrene radical generation contributes after BAG has been used up.

Next, the evolution of average molecular weight and polydispersity index with conversion is summarized for the three systems in Figure 4, graphs a and b, respectively.

The most important feature indicating a certain control of radical polymerizations, the linear increase of molecular weight with monomer conversion, is observed for all photopolymerizations. Only for the photoinitiator-free polymerization the average molecular weight data can be described by two lines with different slopes. The line in the low conversion range up to about 15–20% goes through the origin before the slope diminishes but keeping greater than that for the BAG data which again possessing a greater slope than the BAPO data. This dependence is expectedly inverse compared to the order regarding the rate of polymerization. Accordingly, the number of growing chains is largest for BAPO and lowest for the photoinitiator-free polymerization. It should be mentioned that the data for the polymerizations with BAPO and BAG are nicely reproducible whereas, especially the molecular weight data, for the initiator-free polymerization suffering from quite a huge scatter for different repeats (cf. discussion below).

The results depicted in Figure 4a and 5 indicate that chain transfer is obviously only of minor importance as neither limiting average molecular weights nor limiting molecular weight distributions are reached,¹⁸ even not for the initiator-free polymerization. Consequently, chain stopping occurs predominantly via

Table 2. Initiator Decomposition Rate Coefficient of BAPO and BAG in Ethylbenzene and Styrene at Different Wavelengths

initiator	λ (nm)	371	396	420
BAPO	k_d (h^{-1}) in ethylbenzene	0.40	0.42	0.47
	k_d (h^{-1}) in styrene	0.22	0.17	0.50
initiator	λ (nm)	412	430	450
BAG	k_d (h^{-1}) in ethylbenzene	1.33	1.50	1.47
	k_d (h^{-1}) in styrene	0.62	0.72	0.72

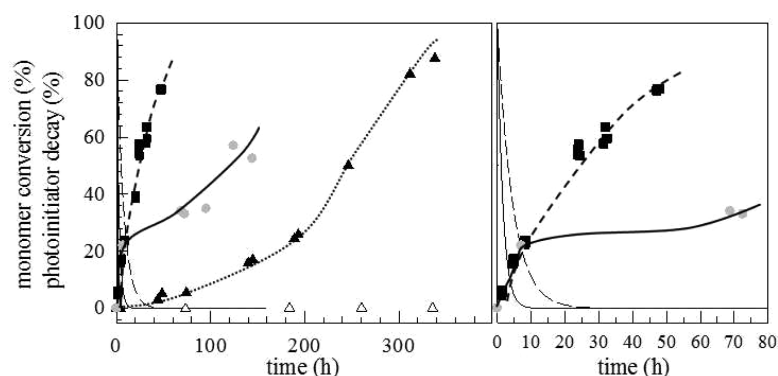


Figure 3. Evolution of the conversion of photoinitiated styrene bulk polymerizations (symbols and lines) and decay of photoinitiators (lines) as calculated from the decomposition rate coefficient in styrene at λ_{max} (cf. data of Table 1); the graph on the right-hand side is an enlarged view of the first 80 hours highlighting the continuation of the polymerization after photoinitiator depletion: (\blacktriangle) with dotted line, without photoinitiator; (\triangle) without photoinitiator in the dark; (\bullet) with solid line, BAG; (\blacksquare) with dashed line, BAPO. The lines in the conversion–time plots are just for guiding the eye.

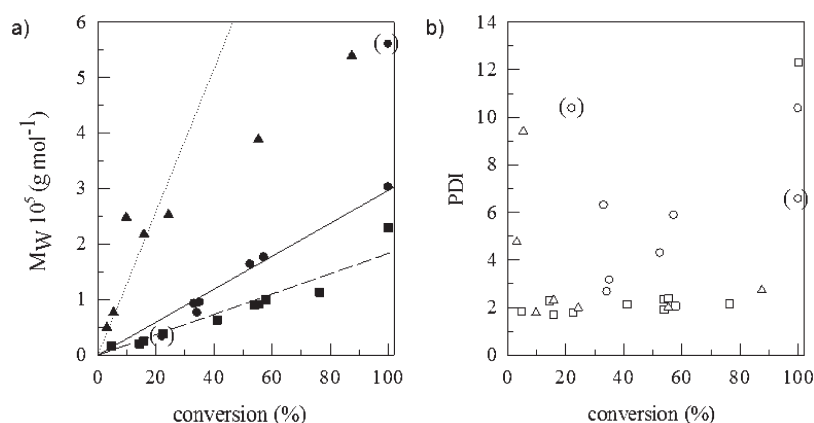


Figure 4. Weight-average molecular weight vs conversion (filled symbols, left) PDI vs conversion (hollow symbols, right): (\blacktriangle , Δ) absence of photoinitiator; (\bullet , \circ) BAG; (\blacksquare , \square) BAPO. The points in brackets denote outliers; the lines represent regressions forced through the origin.

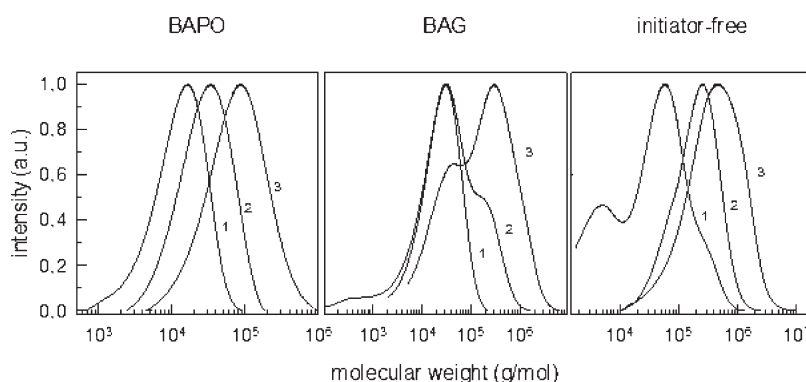


Figure 5. Development of the molecular weight distributions of photoinitiated bulk polymerizations in dependence on the initiating system. BAPO: 1–4, 2–22, 3–76% conversion. BAG: 1–22, 2–33, 3–90% conversion. Initiator-free: 1–5, 2–24, 3–87% conversion.

radical combination under formation of temporarily “dead” chains that can be reactivated again via photochemical radical generation (*vide ante*).

The molecular weight distributions (Figure 5) generally support the idea that these polymerizations might proceed in a controlled fashion. Clearly, the distributions move with increasing conversion toward the high molecular weight region. In addition, the distributions for the polymerizations with BAG seemingly reflect a change in the radical formation mechanism after the consumption of the photoinitiator.

Emulsion Photopolymerization. The transfer of the bulk photopolymerization to an emulsion polymerization requires the addition of water and stabilizer. Thus, the polymerization recipe was modified accordingly using the same molar ratio styrene to photoinitiator, a target solids content of 20 wt %, and a SDS concentration of about 100 mM relative to the aqueous phase which is clearly above the critical micelle concentration. Compared to the homogeneous bulk polymerization emulsion polymerization is characterized by segregated reaction volumes, the monomer swollen latex particles, where monomer conversion takes place predominantly. This is entirely true for classical emulsion polymerization with radical generation in the aqueous phase. However, here we consider photochemical radical generation mainly in the monomer droplets either by the hydrophobic photoinitiators BAG and BAPO or by styrene molecules itself. Under this condition one must consider, beside the latex

particles and the aqueous phase in classical emulsion polymerization, the monomer droplets as another important reaction locus. However, the appearance of the products formed in the monomer phase in the final dispersion depends pretty much on the effectiveness of the stirring which determines the initial droplets size distribution. As we used magnetic stirrer bars the droplets have a pretty broad size distribution and hence, bulk-like polymerization in these drops might lead to coagulum formation. So, at the end of the polymerization we can expect in the given reactor polymeric products originating from two kinetically distinctly different reaction spaces. The reaction products can be easily separated by filtration and discretely analyzed.

Because of the segregation effect causing an effective shielding of active radicals, the polymer molecules grown in the latex particles should possess higher chain length than the polymer found in the coagulum. Moreover and in comparison with bulk polymerization conditions, the overall rate of polymerization should be much higher after particle nucleation has been established the conditions for an emulsion polymerization in the reaction system. The conversion - time curves of Figure 6 clearly show the expected increase in the polymerization rate compared with the bulk polymerization (cf. Figure 3). Obviously, the acceleration of the polymerization reaction due to the segregation effects during emulsion polymerization overrules by far possible losses in the initiation rate due to light scattering caused by monomer droplets and polymer particles. On the other

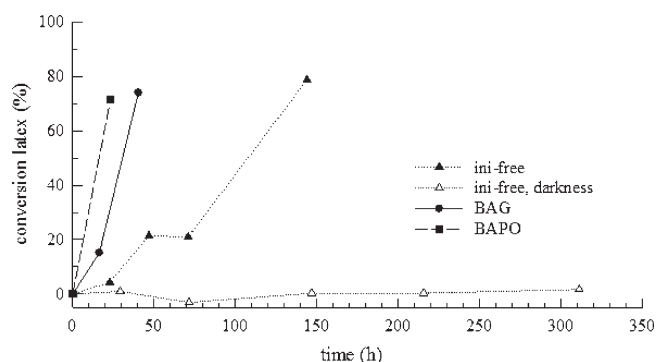


Figure 6. Conversion latex–time curves for photoinitiated emulsion polymerization of styrene in the presence and absence of photoinitiators; the control experiment (ini-free, darkness) proves that within 13 days no styrene conversion takes place; “conversion latex” means the fraction of monomer that has been reacted to polymer and is present in the latex particles.

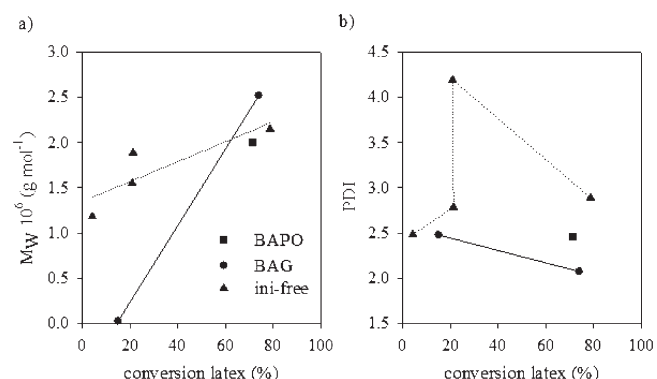


Figure 7. Change of the weight-average molecular weight (M_w , graph a) and the polydispersity index (PDI, graph b) of the polymer isolated from the latex particles with conversion during photoinitiated emulsion polymerization of styrene.

hand, the rate of polymerization follows the same order in dependence on the initiator; i.e., the rate of polymerization is highest for BAPO, a little lower for BAG, and considerably lower for the initiator-free polymerization. The experimental data of the photoinitiator-free run, where the reaction vial was covered with an aluminum foil and no conversion was measurable, proves that indeed with the fluorescence tube as light source photoinitiation takes place. As this kind of fluorescence tubes is used for laboratory illumination, styrene and also other monomers should not be kept in colorless transparent glass ware even not during distillation.

The results of the change of the average molecular weight with conversion for the emulsion polymerizations allow no definitive conclusion whether or not a phototriggered “quasi-living” character is observed under these conditions as well. Even the data for the initiator-free reactions where most samples have been collected due to the much longer duration of the polymerization give only a vague hint that it might be the case.

Interestingly, the average molecular weight of the polymer in the final latex particles depends only weakly on the nature of the initiating systems (Figure 7a). For the bulk polymerizations (cf. Figure 4a); however, this dependence is much more pronounced.

The molecular weight distributions (Figure 8) reveal the expected difference between the polymers isolated from the

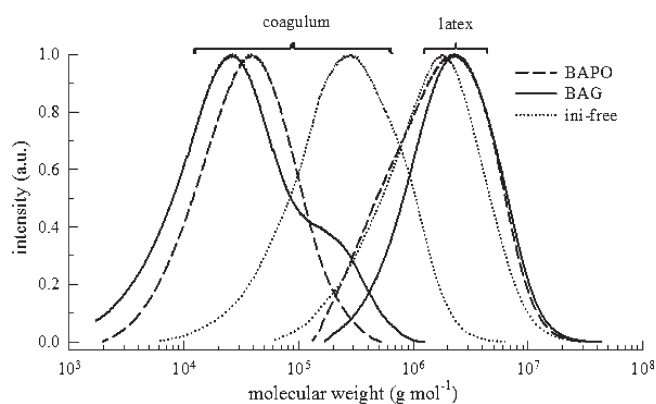


Figure 8. Comparison of the molecular weight distribution of the polymers generated in the coagulum and latex particles for photoinitiated emulsion polymerization of styrene in dependence on the initiating system.

coagulum and the latex particles. The peak molecular weights for the polymers obtained in the presence of both photoinitiators differ by almost 2 orders of magnitude. This difference is for the initiator-free polymerization reduced but still about 1 order of magnitude. So, the molecular weight distribution of the overall polymeric product (latex plus coagulum) for the photoinitiated styrene emulsion polymerization (with BAPO or BAG as photoinitiator) spans a range of 4 orders of magnitude (between 2×10^3 and 2×10^7 g/mol).

The difference in the molecular weight distributions between the polymers in the coagulum and the latex is observed for every repeat of a particular polymerization. Contrary, the order of molecular weights of the polymers in the coagulum and in the latex particles for different photoinitiating systems may vary from repeat to repeat. However, a generally valid finding is that, within a sufficient narrow interval of monomer conversion for repeated polymerizations, the observed spread of the peak molecular weight of the latex polymers is much smaller than that of the polymers in the coagulum. Emulsion polymerization with predominant initiation in the monomer droplets is characterized by the coexistence of two different kinetic regimes leading, regarding the molecular weight, to two different polymeric products.

In addition to the molecular weight, also the morphology of the polymer in the coagulum and the latex phase is significantly different. The average particle size in the latex is mainly determined by the high SDS concentration used in these experiments. However, in comparison to water-soluble initiators where intensity weighted average particle sizes are below 50 nm,¹⁹ the latexes corresponding to the molecular weight distributions depicted in Figure 8 are significantly larger with D_i values of 96.5, 102.5, and 108.3 nm for BAPO; BAG, and initiator-free polymerization, respectively. On electron microscopy images these particles look like ordinary polystyrene particles of spherical shape possessing typical particle size distribution. Essentially, the morphology of the coagulum as depicted exemplarily for the polymerization with BAPO (Figure 9) reflects the very broad sized distribution of the monomer droplets.

The SEM images of Figure 9 reveal that the coagulum is composed of particles in the size range between about 200 μm and 100 nm. The small particles resemble latex particles but they stick tightly to the larger pieces and could not be removed even by repeated washing steps.

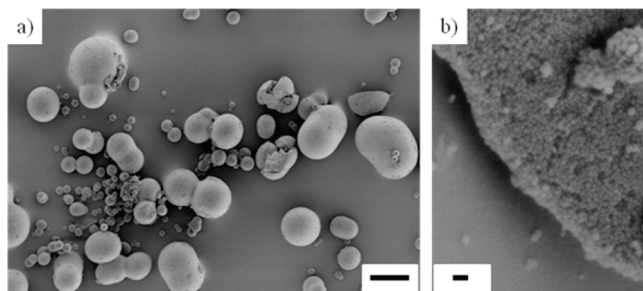


Figure 9. SEM images of the coagulum formed during the photoinitiated emulsion polymerization of styrene with BAPO as photoinitiator: (a) bar indicates 100 μm ; (b) bar indicates 200 nm.

All these observations are directly related to the particularities of the mechanism of emulsion polymerization with predominant initiation in the monomer phase. Radicals generated in the monomer phase will start chain growth almost immediately after leaving the cage. From time to time radicals reach the monomer-water interface and a few of them will be able with a certain probability to surmount the energy barrier and eventually enter the aqueous phase.²⁰ Particle nucleation will take place if the conditions in the aqueous phase, especially regarding the concentration of oligomers, are met. A possible mechanism based on comprehensive experimental studies is discussed in ref 21. In brief, heterogeneous aggregative nucleation is the mechanism that can explain all experimental facts of the process of particle generation. Only after particle nucleation the peculiarities of the emulsion polymerization kinetics are developing where radical segregation is responsible for higher rate of polymerization and higher molecular weight in comparison with bulk kinetics.

In essence, the photoinitiated emulsion polymerization of styrene either with hydrophobic photoinitiators or initiator-free starts in the monomer droplets. We consider here monomer-swollen micelles as tiny monomer droplets. The initiation of the polymerization (radical generation) takes place statistically distributed inside all monomer droplets. Progressing with conversion the emulsion polymerization system is developing and eventually between 80 and 90% of the polystyrene is present in the latex particles.

Contemplations on the Mechanism of Photoinitiation of Styrene Polymerization. The experimental results presented in the preceding sections give strong hints that the photopolymerization of styrene either in the presence or absence of photoinitiators exhibits some unexpected features:

- (1) Bulk polymerization in the presence of BAPO and BAG can be continued even if all photoinitiator is decomposed (cf. Figure 3). Under such condition one would expect within the frame of common radical polymerization kinetics so-called dead end polymerization due to the lack of generation of newly initiating radicals.²² The effect is especially pronounced for BAG where the polymerization continues more than 100 h after photoinitiator consumption.
- (2) The photochemically self-initiated polymerization of styrene (in the absence of photoinitiator) accelerates with time under both bulk and emulsion polymerization condition (Figures 3 and 6). Neither under homogeneous nor under heterogeneous polymerization condition dark polymerization is observed in comparable time (Figures 3 and 6).

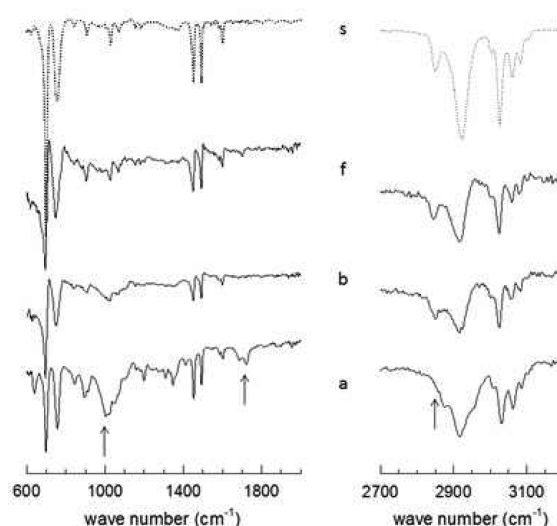


Figure 10. FT-IR spectra of polymers isolated from photoinitiated bulk polymerization in the absence of photoinitiator: (a) product after 3.67 h (almost still zero conversion); (b) polymer after 44 h (3% conversion); (f) final polymer after 338.17 h (88% conversion); (s) standard polystyrene sample for comparison; the arrows mark deviations in sample a from the polystyrene spectrum.

- (3) The average molecular weight increases almost linearly with conversion for all reaction systems during bulk polymerization (Figure 4a). For emulsion polymerization this can only be suspected unambiguously for the photoinitiator-free system (cf. Figure 7a).

These observations lead to the conclusion that the polystyrene chains must somehow participate in the photochemical radical generation in all polymerization systems studied. For the polymerizations in the presence of photoinitiator this should at least be true after BAPO and BAG ceased. If for the polymerizations in the presence of photoinitiators this conclusion is no surprise, due to the specific properties of bisacyl photoinitiators and the corresponding end groups,^{15b,16} it is, however, quite surprising for the photoinitiator-free polymerizations. Obviously, there must be operating a more general mechanism which is until now unrevealed and does not rely on photocleavable initiator end groups.

One reason might be the oxygen that is still dissolved in the monomer. It is known that under oxygen atmosphere a donor-acceptor complex between styrene and O_2 is generated.²³ The charge transfer absorption band is between 320 and 370 nm and upon irradiation the generation of styrene cation and oxygen anion radicals happens. Subsequently, the formation of the cyclobutane dimerization product but also polymerization is observed.²⁴ Moreover, it is also known that polystyrene peroxide decomposes photochemically and is able to restart polymerization.²⁴ It should be noted that we never observed the absorption of the styrene-oxygen donor-acceptor complex in UV-vis measurements for styrene saturated with air.

Indeed, oxygen dissolved in the monomer is an issue for the photoinitiator-free bulk polymerization that has to be considered, at least for the initial period, as proven by the FT-IR spectra of Figure 10. From the sample after 3.67 h despite, that actually no solids content could be measured and hence, the conversion is still close to zero, a spectrum of the product deposited on the aluminum foil during the determination of the solids content

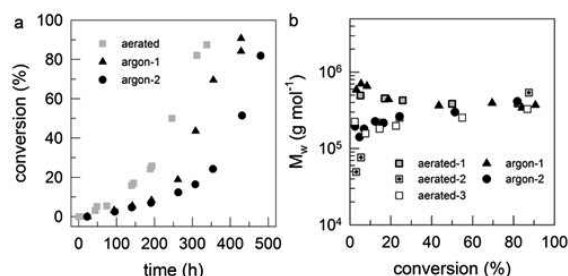


Figure 11. Conversion–time curves (a) and development of the weight-average molecular weight with conversion (b) for initiator-free bulk photopolymerization of styrene under aerated conditions (squares) and argon atmosphere (triangles and dots).

could be recorded. The intense absorption between 1000 and 1100 cm⁻¹ (marked by an arrow) indicates clearly the presence of peroxide units beside styrene in the reaction product.^{24,25} Interestingly, the spectrum of the initial sample shows deviation also in two other regions. Two signals at about 1700 cm⁻¹ can be assigned either to $\nu(\text{C}=\text{O})$ such as in cyclobutane carboxylic acids²⁶ or to isolated double bonds of alkene type.²⁷ Also, the symmetrical stretching vibration of CH₂ in the backbone at about 2850 cm⁻¹ is not visible in the sample taken after 3.67 h (Figure 10b). Already after 3% conversion (after 44 h) the typical polystyrene FT-IR spectrum is recorded and the deviations are not detectable anymore.

The FT-IR spectra show quite convincingly that the initial reaction product (sample a) contains, if so ever, only a minor fraction of polystyrene. The exact chemical structure of this product is not known at the moment. Nevertheless, the conclusion must be drawn that oxygen reacts photochemically with styrene in the beginning of the reaction but the photochemical decomposition of the peroxide cannot be the reason for the observed linear increase of the average molecular weight with conversion during the following 330 h. Remember, the molecular weights are below the chain transfer limit to monomer but increase with conversion which means that repeated radical formation along a given polymeric chain must take place.

Obviously, sound interpretation of the experimental data requires another explanation than photochemical peroxide decomposition to describe the repeated generation of initiating species under participation of dead polymer chains.

Additional hints, that peroxide is an important but not the only source of radical formation come from bulk polymerization where oxygen has been excluded by carefully purging the monomer with argon (cf. Figure 11). Two kinds of experiments with slightly different technical layout have been carried out, one excluding oxygen during the entire duration as best it is possible by maintaining an argon atmosphere (argon-2) and another where during sampling air could slowly diffuse into the vapor phase of the reaction vial (argon-1).

The absence of oxygen causes a substantial decrease in the initial rate of polymerization for polymerization times below 300 h. In the presence of oxygen, the initial rate of polymerization is about a factor of 3 higher. At longer polymerization times the rates of polymerization getting closer despite the composition of the gas phase in the reaction vials (Figure 11a). In contrast to the conversion time curves, the conversion dependence of the average molecular weight (Figure 11b) shows no clear relationship with the composition of the gas phase. Up to about 40–50%

of conversion the experimental data either increase or decrease with conversion. At conversion higher than 50%, the scatter is considerably reduced and the all data points follow within the experimental error the same curve with slightly increasing molecular weight.

Photochemical radical generation in the absence of photo-initiators is possible via photo electron transfer (PET) between the donor–acceptor pair. It should be noted that under exergonic conditions PET necessarily leads to the formation of radical ions (acceptor radical anion and donor radical cation).²⁸ For the photoinitiator-free styrene bulk polymerization the only remaining donor–acceptor pair, after oxygen has been either consumed or excluded, is styrene – polystyrene. Assuming that ethylbenzene is a good model for polystyrene regarding the UV–vis absorption as proven in²⁹ the spectral information on Figure 13 suggest that styrene monomer might act as donor for an excited repeating unit in polystyrene. In addition, quantum mechanical calculations show that conjugation and the transient configuration during the approach of the reactants cause a significant shift of the occupied and unoccupied orbitals of the acceptor and donor.³⁰ Moreover, the excited states of olefins have twisted geometry which can be either diradicaloid or zwitterionic in nature.³¹ The styrene radical cation has two absorption bands, one at about 350 and a second at about 600 nm as proven by laser flash photolysis studies.³² It is also known that irradiation of styrene at 254 nm in neutral water causes the formation of the 1-ethyl carbocation which is eventually transformed to the 1,1-phenylethanol.^{31b}

In addition, it is also possible that the polymerization is initiated by styrene diradicals as discussed in.¹³ The diradicals are formed in the triplet state which is occupied via intersystem crossing from the excited singlet state during UV irradiation. Experimental data show that styrene can act under UV-irradiation as a kind of initiator for the photografting reaction of acrylic acid onto polyethylene.¹³

Mechanism of Radical Formation—What Is the Initiating Species? The available information can be used to construct a simplified energy diagram (Figure 12a) that explains the PET based on experimental data of the UV–vis absorption spectra (Figure 13) and ionization potential of ethylbenzene³³ and styrene.³⁴ A possible reaction sequence as sketched in Figure 12b assumes after PET hydride transfer from the polystyrene radical anion to the styrene radical cation and the formation of two polymerizable radicals, a polymer radical and a styrene radical which structure cannot further specified at the moment. Hydride transfer is well-documented in organic chemistry.³⁵

To prove the mechanism of radical formation by identifying the end groups in the polymer prepared in the absence of photoinitiators is challenging, as the molecular weight is high. Nevertheless, after careful control experiments excluding other sources such as impurities in solvents or residual monomer, ¹H NMR spectra give hints to CH₃ groups belonging to the polymer (Figure 14). However, it was not possible to confirm the existence of methyl groups by ¹³C NMR spectroscopy.

Interestingly, also the polymers prepared in the presence of BAPO and BAG show signals in the same range of chemical shifts (δ = 0.915 ppm for the center peak). This is, on the one hand, astonishing as one might expect predominantly initiator end groups (for BAPO mainly 2,4,6-mesityloyl end groups at higher conversion). On the other hand, PET according to the mechanism of Figure 12b should happen as well, especially during the later stages of the polymerization after consumption of the

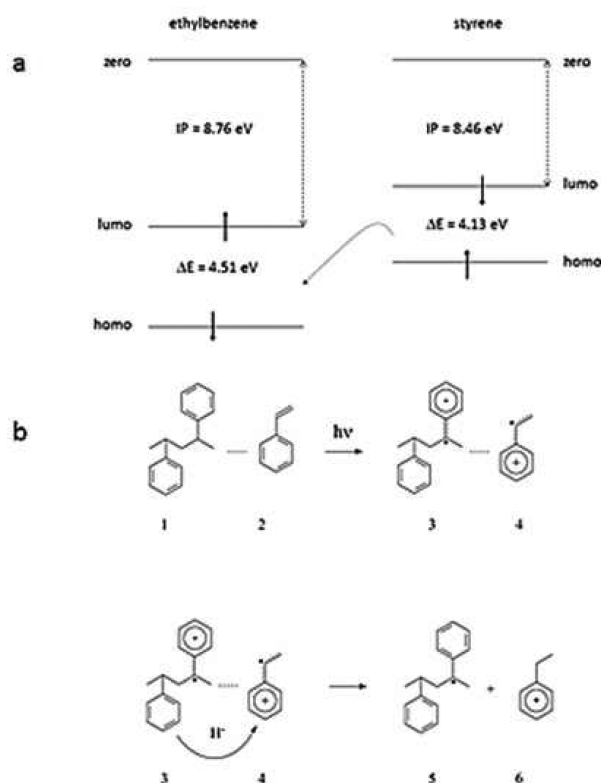


Figure 12. (a) Simplified energy levels of ethylbenzene as model for polystyrene and styrene based on experimental data of the ionization potential (IP) and UV–vis absorption (cf. Figure 13) showing that PET between a repeating unit in polystyrene and styrene monomer is possible, (b) PET between a repeating unit of polystyrene (1) and styrene monomer (2) leading to a radical anion in the polystyrene chain (3) and a styrene radical cation (4) with subsequent hydride transfer and formation of a radical in the polystyrene chain (5) and styrene radical (6).

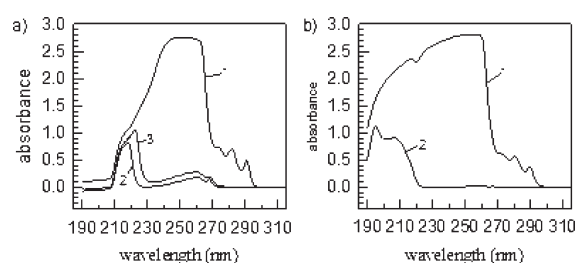


Figure 13. UV–vis absorption spectrum of styrene (1), ethylbenzene (2), and polystyrene (3) in THF (graph a) and water (graph b).

photoinitiator. The ^1H NMR spectra of all polymers (Figure 14) possess a triplet in the region between 0.88 and 0.94 ppm, which is assigned to a methyl group in neighborhood to a methylene group. Consequently, the initiating species is either a polystyrene or/and an ethylphenylene radical (structure 5 and 6 of Figure 12b). The exact position of the radical at the phenyl ring cannot be specified at the moment. This is an unexpected result and needs to be verified in future studies. Even if the initiation of chain growth starting from the phenyl ring is slow, it is, however, possible.³⁶ Despite the need to get further experimental evidence, the reaction sequence of Figure 12b explains the occurrence of

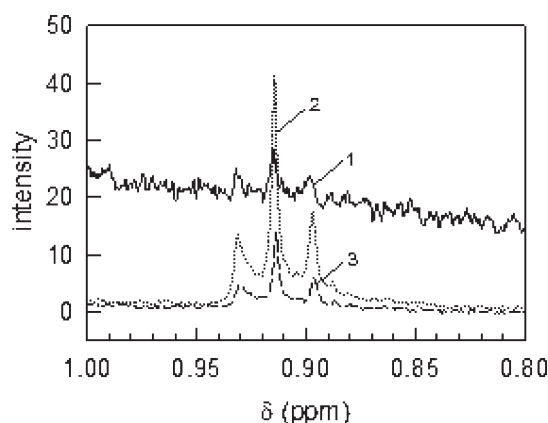


Figure 14. Methyl proton region of the ^1H -NMR spectra of polystyrene homopolymers prepared via bulk polymerization in the presence of BAPO (spectrum 1 stretched by a factor of 10) or BAG (spectrum 2) or photoinitiator-free (spectrum 3). Concentration for all polymers 20 mg of precipitated polymer per mL of CDCl_3 .

CH_3 -terminal groups and is in accordance with the ^1H NMR data. Note, in ref 37, a reaction sequence is proposed that starting from the photoinitiated styrene diradical leads after addition of styrene monomer to a tail-to-tail diradical dimer which after chain transfer to a styrene monomer disproportionates into an unsaturated dimeric radical and a styrene head radical with a hydrogen terminal group. Formation of the latter radical is also proposed in ref 13 as the result of chain transfer of the styrene tail-to-tail diradical dimer with polyethylene. Methyl end groups are also postulated for another initiation mechanism, i.e., for the thermal initiation of styrene polymerization with hydroperoxides.³⁸ However, in none of these papers^{13,37,38} is experimental evidence, i.e., analytical data, provided for the proposed structure.

The intensity of the CH_3 signal (Figure 14) changes in the order BAPO < photoinitiator-free < BAG and can be understood considering mainly the average molecular weight of the polymers, which follows the reverse order (cf. Figure 4a). Obviously, the initiation efficiency of the photoinitiator is only of marginal influence.

The assumed PET mechanism of radical generation leads also to polymeric initiating radicals. Hence, it can explain the observed increase of the molecular weight with conversion and the acceleration in the photoinitiator-free and the later stage of the BAG-initiated polymerization as termination is more and more reduced with increasing molecular weight of the initiating radicals. However, this mechanism can also lead to branched polymers since PET must not happen only with a repeating unit close to the chain end of the polymer. Branching that occurs randomly along a polymer chain might explain the observed differences in the conversion dependence of the average molecular weight (Figure 11b). On the other hand, the ultimate state of branching, gel formation, has never been observed during our experiments. Very likely, the gel effect prevents very effectively the termination between branched polymer chains.

A surprising piece of information comparing the data of Figure 13 and Figure 1 is that the absorption of the presumably active species is very much on the edge of the lamp spectrum. Presumably this is the reason for the quite low rate of polymerization of the photoinitiator-free polymerization under this particular irradiation condition. Despite the slowness, it is experimental fact that the styrene polymerization in both bulk

and emulsion polymerization can be started photochemically in absence of photoinitiator even with a normal fluorescence tube.

SUMMARY

Photopolymerization of styrene with initiation in the monomer phase is under homogeneous and heterogeneous conditions as bulk and emulsion polymerization, respectively, characterized by essentially the same features with respect to radical formation and chain growth. In either case the polymerization can be started photochemically with normal fluorescence tubes as light source which are also used for indoor illumination.

The rate of polymerization is, independent of the polymerization procedure, highest for BAPO, lower for BAG, and lowest in the absence of photoinitiator. Despite predominant radical generation in the monomer phase, emulsion polymerization proceeds smoothly and the expected increase in the rate of polymerization, compared with bulk polymerization, is observed. Moreover, the molecular weight of the polymer in the latex particles is about 1 order of magnitude higher than the polymer found in the coagulum of emulsion polymerization or generated in bulk polymerization.

The bulk polymerizations in the presence of photoinitiators continue even after complete decomposition of BAG and BAPO without the effect of dead end polymerization is being observed. For BAPO initiated polymerization this is the expected behavior as photodecomposition of phosphine oxide chain ends entails continuous generation of initiating radicals.^{14,15b} For BAG, this effect seems less pronounced but nevertheless the bulk polymerization goes on for more than 100 h after complete photoinitiator consumption, interestingly, with increasing rate as also observed for the photoinitiator-free polymerization over the entire duration.

The average molecular weight increases, independent of the polymerization procedure (at least unambiguously proven for the photoinitiator-free polymerizations) and recipe, with monomer conversion suggesting a certain kind of “photocontrolled” chain growth.

Taking all experimental results together, we suggest that a photo electron transfer reaction between a styrene monomer and a repeating unit in the polystyrene chain leads repetitively to generation of radicals (actually radical ions) ensuring both polymerization in the absence of photoinitiator and increasing molecular weight with conversion.

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