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Correlation between Polystyrene Molecular Weight and Initiator Properties in Microemulsion Polymerization

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ABSTRACT: A series of anionic organic peroxides were synthesized and used to create polystyrene nanoparticles in sodium dodecyl sulfate and dodecyltrimethylammonium bromide microemulsions. A plot of log(polymer molecular weight) vs log O/W partition coefficient is linear with a slope of −0.9 for initiators that have similar free radical generation efficiencies, suggesting that very few of the free radicals from peroxide solubilized in water react with monomer to form polymer. This indicates that the radicals formed at the interface are far more effective in initiating the polymerization than those generated outside the microemulsion droplets.

Introduction

There has recently been a great deal of interest in using a transparent microemulsion system to generate polymers.[1−10] These are transparent one-phase systems; however, on a microscopic level, there are small oil droplets on the order of dozens of nanometers. These systems have the advantage of forming smaller particles[11] with simpler spectroscopic properties[8] than emulsion systems. In the case of photoreactions, microemulsion systems allow exact control of the timing of the reaction by the control of the light.[7] There is a wide range of free radical initiators designed to form radicals when exposed to light of an appropriate wavelength[9,12−15] to take advantage of such transparent systems.

With monomer segregated to the microemulsion droplets, transfer of radicals between the water and monomer is very important. Various water-soluble and oil-soluble initiators are used industrially to place the radical-producing species with either the monomer or the solvent.[16] Recently, there have been a handful of polymerization studies where the initiator is a species that sits at the interface between the droplets and the water.[9,13,14,17−19] All of these myriad initiators are intended to affect the polymerization process by controlling the location of the radical initiator.

For water-soluble initiators, the accepted mechanism of initiation in microemulsion polymerization of styrene is that the free radicals are generated in water and then diffuse to the microemulsion droplets to start the polymerization.[5,20−30] It has been demonstrated that styrene is not initiated in solution to any appreciable extent, and as the initiator is water-soluble, free radicals will not be produced in the micelle.[5] Conceptually, this is an inefficient process. Radicals are expected to have a very short lifetime due to their reactivity and are unlikely to survive very long in their original form. Time spent diffusing into a micelle is possibly long enough for a large fraction of the radicals to be quenched. The interfacial initiators are intended to avoid this problem.[9,13,14,17−19]

The idea that a compound is restricted to either the microemulsion droplets or the water is somewhat simplistic, however. In a system with two distinct phases, such as an oil/water mixture, a third component will partition between the two phases.[31] Even highly nonpolar molecules, such as polycyclic aromatic hydrocarbons, have slight solubility in water.[32] Even though the microemulsion is not macroscopically a two-phase system, there are distinct microdomains, and partitioning between them will occur. Highly water-soluble compounds will have a slight solubility in the hydrated layer of a micelle, and there will be partitioning between the aqueous domain and the hydrated surfactant layer of the microdroplet. Generally, individual radicals located in the micelle would be more likely to initiate a polymerization than that in the aqueous domain, due to the proximity of the monomer. If that is the case, a more hydrophobic initiator will produce more radicals in a position to form polymer, leading to more polymer chains and a lower molecular weight.

In this paper, a series of anionic peroxide-based phthalic anhydride derivatives were synthesized and used to initiate styrene polymerization in sodium dodecyl sulfate or dodecyltrimethylammonium bromide microemulsions. The key objective of this study is to identify correlations between the solubility of the peroxides and the polymer molecular weights obtained. As these are all very water-soluble peroxides, it is expected that the concentration of peroxide in the styrene microdroplets will be very small. If a major source of radicals for polymerization is from the solvent, there will be no correlation between the molecular weight of the polymer formed and the solubility of the peroxide in the micelle. If the initiator partitioned into the micelle or at the interface is a significant source of radicals, the molecular weight of the polymer formed will depend on the partitioning of the peroxides.

Experimental Section

General. All water was distilled using a Barnstead water purification system. Styrene (Aldrich Chemical) was extracted with aqueous base to remove the inhibitor and distilled under vacuum. The distilled styrene was refrigerated and used within 1 month of distillation. Polystyrene molecular weight standards were purchased from Phenomenex. HPLC grade tetrahydrofuran was manufactured by JT Baker and purchased from VWR scientific. All other chemicals were purchased from Aldrich chemical and used as received.

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Charge distribution calculations were performed using Spartan molecular modeling software (version 5.0.3GL). All calculations were done using a semiempirical AM1 model with geometry optimization.

UV kinetics data were gathered with a Perkin-Elmer Lambda 6 UV spectrometer equipped with a Precision Scientific model 66600 temperature controller. NMR spectra were collected with a Brukner AC250 spectrometer. ^{1}H NMR data are reported as δ values in ppm from tetramethylsilane. Polymer molecular weight was determined by gel permeation chromatography using a Hewlett-Packard series 1050 HPLC system with a Phenomenex phenogel 5 × 104A gel permeation column. Tetrahydrofuran was used as the eluent. Calibration with polystyrene standards was done every day to minimize drift. HPLC data for octanol/water partition coefficients were run on a Hewlett-Packard 1050 HPLC system using a Vydac C18 column and a Varian Star 9049 refractive index detector. An isocratic 90:10 water:methanol mixture was used to elute the compounds.

Microemulsion Polymerization. Polymerization experiments used 0.4 g (0.44 mL) of styrene, 1.5 g of surfactant (either sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium bromide (DTAB)), 8.5 g of distilled water, and 2×10^{-5} mol of initiator, all placed into a 10 dram vial and sealed with a sleeve septum. Samples were purged with nitrogen for 15 min. They were then held at 80 °C for 1 h in an oil bath with constant stirring. The resulting solution was immediately poured into 150 mL of ethanol to precipitate out the polymer and gravity filtered through fluted filter paper. A 100 mL aliquot of water was then poured through the filter pack to remove excess surfactant, followed by 100 mL of ethanol to remove unreacted styrene. The polymer was dried in a vacuum desiccator for at least 24 h.

To examine the effect of initiator concentration, a series of runs using phthalate peroxide at different concentrations were run. These were done using the same conditions as above, using SDS as the surfactant, and using peroxide concentrations of 1, 2, 2.5, 3, and 4 mM.

Radical Trapping. Free radical generation was determined by reaction with *p*-nitrosodimethylaniline (PNDA). 0.563 g (3.75×10^{-3} M) of PNDA was mixed with water to make 100 mL of solution. This solution was diluted 100/1 in water to make a 3.75×10^{-4} M solution. 20 mL of this PNDA solution was mixed with 12.5 g of SDS and diluted to 250 mL, creating a solution 3×10^{-5} M in PNDA and 5% (w/w) in surfactant. 4 mL of this solution was mixed with 4×10^{-4} mol of peroxide. Samples were purged 10 min in a cuvette sealed with a septum. The samples were then placed in a spectrometer with the temperature controlled to 80 °C and monitored at 440 nm for 3 h.

Synthesis. Each peroxide compound was synthesized from the appropriate phthalic anhydride derivative, using the sodium salt of *tert*-butyl hydroperoxide. For most of the peroxides, it was possible to find a solvent that the peroxide was sparingly soluble in to allow purification by filtration. For the peroxide where this was not possible, chromatography was used.

2,3-Naphthalenedicarboxylic Anhydride. A solution of 2,3-naphthalenedicarboxylic acid (1.38 g, 6.0 mmol) in acetic anhydride (20 mL) was heated for 2 h under reflux. On cooling, a light brown precipitate formed. The precipitate was filtered and washed with acetic acid to give 1.1 g of pale brown solid. Yield 92%; mp 242−244 °C. ^{1}H NMR ($CDCl_3$): δ 8.6 (s, 2H), 8.2 (doublet pair, 2H, $J = 4, 6$ Hz)) and 7.8 (doublet pair, 2H, $J = 4, 6$ Hz).

2-Carboxy-3-tert-Butyldioxynaphthalenecarboxylate, Monosodium Salt (Naphthyl Peroxide). To a solution of 2,3-naphthalenedicarboxylic anhydride (0.18 g, 0.9 mmol) in acetone was added *tert*-butyl hydroperoxide, sodium salt (0.11 g, 0.95 mmol), and stirred for 4 h at room temperature. A solid formed during the reaction. The precipitate was filtered, washed with acetone, and dried under vacuum to give 88 mg of white solid. Yield 31%; mp darkens without melting at 165 °C. ^{1}H NMR (D_2O): δ 8.2 (s, 1H) 8.0 (s, 1H), 7.9 (doublet pair, 2H, $J = 4, 7$ Hz) 7.6 (m, 2H, 9 Hz), and 1.4 (s, 9H).

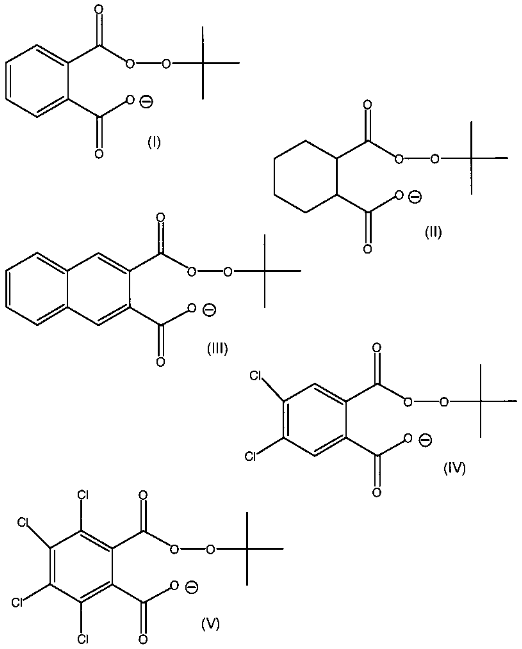

Figure 1. Peroxide initiators used in this study.

2-tert-Butyldioxycyclohexanedicarboxylic acid, Monosodium Salt (Cyclohexyl Peroxide). To a solution of 1,2-cyclohexanedicarboxylic anhydride (162 mg, 1.0 mmol) in acetonitrile (4 mL) was added *tert*-butyl hydroperoxide, sodium salt (0.12 g, 1.05 mmol), and stirred for 10 h at room temperature. A solid forms during the reaction. The precipitate was filtered, washed with acetonitrile, and dried under vacuum to give 168 mg of white solid. Yield 63%; mp darkens without melting at 215 °C. ^{1}H NMR (D_2O): δ 3.0 (q, 1H, $J = 5$ Hz) 2.7 (q, 1H, $J = 5$ Hz), 1.9 (m, 2H, $J = 7$ Hz), 1.7 (m, 2H, $J = 6$ Hz), 1.4 (m, 4H, $J = 9$ Hz) 1.3 (s, 9H).

2-tert-Butyldioxy-4,5-Dichlorophthalic Acid, Monosodium Salt (Dichloro Peroxide). To a solution of 4,5-dichlorophthalic anhydride (221 mg, 1.0 mmol) in acetonitrile (30 mL) was added *tert*-butyl hydroperoxide, sodium salt (0.12 g, 1.05 mmol), and stirred for 4 h at room temperature. The solid formed was filtered out and dissolved in methylene chloride. Column chromatography (methylene chloride:methanol 4:1 on silica gel) gave 100 mg of white solid. Yield 32%; mp > 300 °C. ^{1}H NMR (D_2O): δ 7.9 (s, 1H) 7.7 (s, 1H) and 1.4 (s, 9H).

tert-Butyldioxyphthalic Acid, Monosodium Salt (Phthalate Peroxide). To a solution of phthalic anhydride (0.74 g, 5.0 mmol) in acetonitrile (45 mL) was added *tert*-butyl hydroperoxide, sodium salt (0.59 g, 5.3 mmol), and stirred for 5 h at room temperature. The solid formed was filtered, washed with acetonitrile, and dried under vacuum to give 0.78 g of white solid. Yield 60%; mp > 300 °C. ^{1}H NMR (D_2O): δ 7.7 (d, 1H, $J = 7$ Hz), 7.6 (t, 1H, $J = 7$ Hz), 7.5 (d, 1H, $J = 8$ Hz), 7.4 (doublet pair, 1H, $J = 7, 8$ Hz), 1.3 (s, 9H).

2-tert-Butyldioxy-3,4,5,6-tetrachlorophthalic Acid, Monosodium Salt (Tetrachloro Peroxide). To a solution of 3,4,5,6-tetrachlorophthalic anhydride (0.3 g, 1.0 mmol) in acetonitrile (45 mL) was added *tert*-butyl hydroperoxide, sodium salt (0.12 g, 1.05 mmol), and stirred for 5 h at room temperature. The precipitate was filtered, washed with acetonitrile, and dried under vacuum. The solid was suspended in solvent (methylene chloride:methanol 1:1), sonicated for 1 h, and then filtered. The filtrate was dried under vacuum to give 98 mg of white solid. Yield 33%. ^{1}H NMR (D_2O): δ 1.4 (s).

Results and Discussion

Five anionic organic peroxides were synthesized and characterized as described in the Experimental Section. Figure 1 lists the structures of these peroxides. Using the phthalate peroxide (**I**) as a reference point, the cyclohexyl peroxide (**II**) was included to examine the difference between an aromatic system and its aliphatic counterpart. Similarly, the naphthyl peroxide (**III**) is to demonstrate the impact of an extended aromatic system. Additionally, dichloro- and tetrachlorophthalate peroxides (**VI** and **V**) were included to examine the influence of electronic and steric factors. In addition, the peroxides in this set have different polarity and size.

There are a fairly large number of factors that affect molecular weight in microemulsion polymerization. In the styrene microemulsion, essentially all the monomer is in swollen micelles, with very little floating free in solution, due to the low solubility of styrene.[47] With the small size of the micelles, diffusion of monomer is a very rapid process, even with such low monomer solubility. Some of the monomer droplets are initiated by a free radical and start to form polymer. Diffusion from the uninitiated droplets causes these initiated particles to grow larger than the original droplets.[3] At some point, the growing polymer chain transfers the free radical to another droplet, and the process starts over again.[6,24,37−39] The reaction ends when the free radical chains are killed by various free radical termination reactions, or the styrene is completely consumed. Changes in the amount of surfactant or monomer (affecting droplet size), initiator (changing number of particles initially initiated), or trace amounts of impurities (affecting radical quenching and transfer) all affect molecular weight. In this study, for the main experimental work, only the species of the initiator is changed. All other factors are, as close as possible, held constant.

Microemulsion polymerization was conducted according to a procedure reported earlier.[9,19] Before polymerization, the microemulsions were clear solutions with a viscosity slightly greater than that of water. These microemulsions were stable; no reaction or precipitation was noticed upon sitting at room temperature for several hours. The latex suspensions formed from polymerization were cloudy with a blue tint from light scattering. Because of the large amount of surfactant in the microemulsion, it was necessary to use a low nitrogen flow rate when degassing the samples and a vial that was much larger than required to hold the liquid to prevent losses from foaming.

As is common for microemulsion polymerization,[4] the molecular weight for all the polymerizations was rather polydispersed, with $M_w/M_n \sim 3.5-4$ for all the polymerizations run. In all cases, the molecular weight used in the plots was that corresponding to the elution time of the maximum signal in the GPC plot which was almost identical to M_n.

Except for peroxide (**II**), the larger and bulkier the initiator, the lower the molecular weight of the polystyrene formed. This suggests that partitioning between the microemulsion droplets and the aqueous phase is an important factor in determining molecular weight. The larger the initiator, the less hydrophilic it will be and the more it will partition into the hydrated layer of the microemulsion droplet.

To quantify this, some way of measuring at least the relative partitioning of the peroxides is needed. Imagine two compounds, one more hydrophobic than the other. Regardless of what chemicals make up the two phases they are partitioning between, the first compound will partition more into the hydrophobic phase than the other, assuming no specific interactions or reactions. This indicates that partitioning is a measure of hydrophobicity and that examining the partitioning with a standard solvent pair will give relative partitioning data for any other solvent pair. It can be shown thermodynamically that logarithm of a partition coefficient in one solvent pair will be proportional to the logarithm of the partition coefficient of the same solute in any other solvent pair.[31,40] Traditionally, octanol and water are the solvents used to measure a “standard” partition coefficient.[41−44] This can be correlated to most partitioning phenomenon, such as HPLC behavior,[33] bioavailability,[43] bioaccumulation,[45] environmental transport phenomenon,[41] and even drug effectiveness.[44]

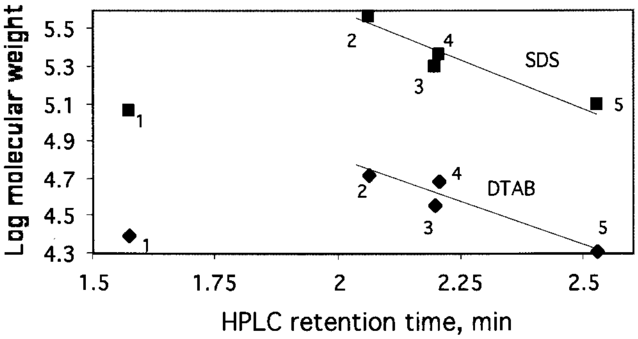

Figure 2. Plot of log MW vs initiator HPLC retention time. The peroxide initiators are cyclohexyl (1), phenyl (2), naphthyl (3), dichlorophthalate (4), and tetrachlorophthalate (5) as labeled on the plot. Symbols: ■, polymerizations using SDS; ◆, polymerizations using DTAB.

Figure 2 is a plot of the log molecular weight vs HPLC retention time. HPLC retention time is linearly related to the log of the octanol/water partition coefficient.[33] Ignoring the first point (the lowest O/W partition coefficient, peroxide (**II**)), the points form a linear trend, with the more hydrophobic peroxides giving lower molecular weights. The polystyrenes made from DTAB microemulsions have a lower molecular weight polymer than the polymers made from SDS solution, but the plots are, within the accuracy of the measurements, parallel, with a slope of −0.9.

It can be assumed that a compound placed in this system will partition between the microemulsion droplets and the aqueous solvent. While the synthesized peroxides, with their anionic charge, are all very water-soluble, some are more hydrophilic than others. It would stand to reason that the less hydrophilic initiators would spend more time in the micelle than the more hydrophilic peroxides. The higher the concentration of peroxides at the micelle, the closer the radicals formed will be to the monomer. This means less free radicals are lost to side reactions, and more start polymer chains, leading to a lower molecular weight per chain.

The explanation for the different surfactants leading to different molecular weights also falls on a partitioning explanation. All these peroxides have a negative charge. By Coulombic attraction, there would be more of the peroxide near the positively charged DTAB micelles than negatively charged SDS micelles. In essence, the Coulombic forces modify the partition coefficient. The attraction of the DTAB causes more of the initiator to be in the environment of the micelle, leading to a larger partition coefficient for the peroxide than that of a neutral micelle. The negative charge on the SDS has the exact opposite effect, repelling the initiator from the area of the micelle. A nonionic surfactant would be expected to produce a polymer with a molecular weight somewhere in between the molecular weights produced from the SDS and DTAB microemulsions.

The steep slope of the log O/W partition coefficient vs polymer molecular weight is quite surprising. These are all very water-soluble peroxides; it is to be expected that most of the peroxide would be in the water domain. If it is assumed that a proportion of all the radicals formed in the solution will diffuse to a micelle and that every radical that enters a micelle (either from the solution or from generation at the micelle) forms a polymer chain, it is possible to make some qualitative explanations of these results.

Obviously, if all the radicals formed in solution enter micelles and start polymer chains, the O/W partition coefficient will have no influence on the molecular weight of the polymer formed. Under that assumption, each radical formed has the exact same probability of forming a polymer chain, regardless of where it formed. In other words, if the accepted mechanism of free radical diffusion from the aqueous phase holds, the molecular weight of polymer will not be dependent on the partitioning of the initiator.

The case where every free radical generated in water is removed by mechanisms other than polymer formation will give a slope of -1 to the log O/W vs log MW curve. This assumption is equivalent to assuming that all the radicals formed at the interface form polymer, while all the others are consumed by nonpolymerization reactions. More realistic assumptions would include recombination and other radical quenching reactions at the micelle, leading to a log O/W vs log MW curve with a slope of less than one. The experimentally determined curve has a slope of -0.9. This strongly suggests that few if any of the radicals formed in the aqueous solution are involved in polymerization.

In an attempt to determine how much of the missing 0.1 of slope is due to free radical transfer from the solution and how much is due to radical recombination and other mechanisms, a series of experiments using different peroxide concentration were run, using phthalate peroxide and SDS. Increasing the O/W partition coefficient increases the amount of peroxide at the micelle/aqueous interface. Another way of doing the same thing would be to increase the amount of peroxide in the system. The O/W partition coefficient is the concentration of a substance dissolved in octanol divided by the concentration of the same substance dissolved in water, when the octanol and water are in equilibrium. Doubling the O/W partition coefficient does not necessarily mean that the amount of the substance in the organic phase will be doubled. However, if the O/W partition coefficient is small, an increase will involve a relatively large increase of the substance in the octanol phase percentagewise, with a small decrease in the amount in the water phase, percentagewise. All these peroxides are very water-soluble; it is expected that the numeric value of the O/W partition coefficient will be very low. This means that almost all of the change is due to change in the concentration of the octanol phase, while the concentration of the water phase will be almost constant. We can thus compare a log initiator concentration vs log molecular weight plot directly to the HPLC retention time vs log molecular weight plot.

Figure 6 is a plot of the log of the concentration of the phthalate initiator vs the log of the molecular weight of polymer produced. This plot has a slope of -0.91. Within the accuracy of the plots, this is identical to the slope of the log molecular weight vs HPLC retention time plot. This means that none of the free radicals formed in the solution are involved in polymerization; only the ones from the interface form polymer.

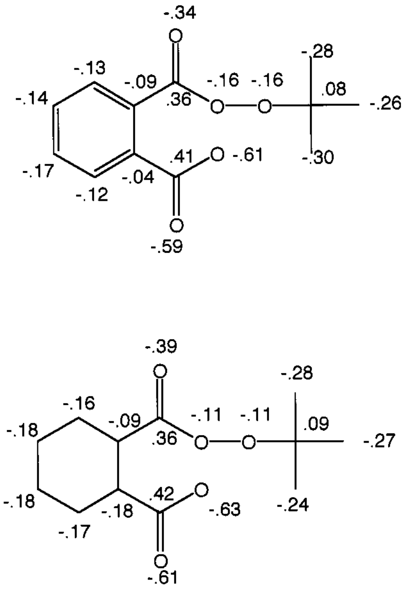

Figure 3. Calculated charge distribution of the phenyl and cyclohexyl initiators. Hydrogens have been omitted for clarity.

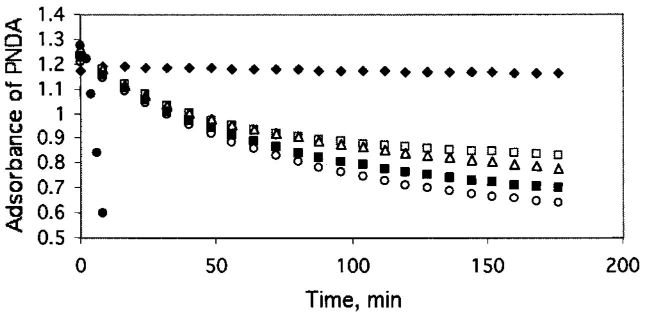

Figure 4. PNDA adsorbance vs time with peroxide initiator. Only the first four points for the cyclohexyl initiator appear on this scale. Symbols: ◆, PNDA control; □, phenyl peroxide; △, naphthyl peroxide; ■, tetrachloro peroxide; ○, dichloro peroxide; ●, cyclohexyl peroxide.

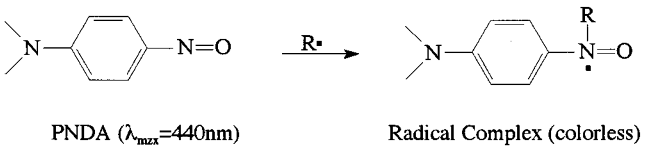

Figure 5. Reaction of PNDA with a radical.

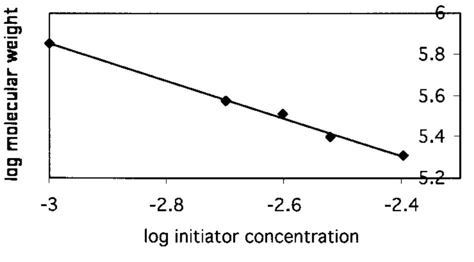

Figure 6. Variation of polymer molecular weight with peroxide concentration using phthalate peroxide.

There are few possible explanations for the severe deviation of the cyclohexyl peroxide from the trend. It was assumed that the number of polymer chains is proportional to the number of free radicals from the peroxide that make it to the micelle and that chain termination reactions are very similar between the different initiators. With these assumptions, the possible differences in peroxides are limited differences in the amount of radical formed or differences in where the radical is formed.

Peroxy compounds are, in general, rather inefficient in producing free radicals in polar solvents. The bond has a tendency to cleave heterolytically or rearrange to a nonperoxide species, which produces ions and rearrangement products rather than radicals.[9] Hydroperoxides almost exclusively cleave heterolytically without a catalyst.[9,18] Dialkyl peroxides are more efficient at producing radicals, but still, the vast majority of peroxide decomposition reactions form nonradical products. It is possible that the nonaromatic peroxide will cleave homolytically more frequently than the aromatic one.

The amount of free radicals generated by the peroxides was determined by a trapping procedure. While most free radicals are very reactive, those based on nitrogen–oxygen type functional groups are more stable.[17,34,35] Indeed, some of these radicals are stable enough to go though organic reactions without involving the radical.[34] *p*-Nitroso-*N*,*N*-dimethylaniline (PNDA) was used as a trap for the radicals formed by the cleavage of the initiators. It is a strongly colored chemical ($\lambda_{\max} = 440$ nm, $\epsilon = 34\,200$), which forms a stable complex with hydroxyl radicals[35,36] that is nearly colorless at that wavelength[36] (Figure 5). While this chemical has not been used to trap radicals other than hydroxyl radical, similar chemicals have been used to trap radicals for electron spin resonance studies. Experimentally, it is noted that the PNDA slowly decays in light (ref 36 and Figure 4). This is zero-order kinetically and is probably a photochemical reaction from the light from the spectrometer. This was taken into account when calculating free radical generation efficiency.

The results of the reaction between the initiators and PNDA are shown in Figure 4. Cyclohexyl peroxide shows all the data points. For the other peroxides, only every forth data point is shown for clarity. It is obvious that the cyclohexyl initiator is much more efficient at producing radicals than the other initiators. Compared to the phthalate peroxide, the naphthyl was 1.2 times as efficient at producing radicals, the dichloro and tetrachloro peroxides were 1.3 times as efficient, and the cyclohexyl peroxide was 20 times as efficient. This was calculated by determining how much PNDA was reacted at 3 h, extrapolating how much of that was due to the zero-order decay of PNDA in light, and assuming the remaining PNDA consumed was the amount of free radical generated. It was necessary to rerun the cyclohexyl peroxide at a lower peroxide concentration to make this calculation, as using the same concentration as the other peroxides lead to all the PNDA being consumed. While all the aromatic compounds are roughly equivalent in the amount of homolytic cleavage, especially considering the small amount of peroxide measured out and the resulting uncertainties in the concentration, the cyclohexyl derivative cleaves homolytically an order of magnitude more frequently. While there is not a direct inverse relationship between the number of radicals and the molecular weight,[23] it is reasonable to assume that an order of magnitude increase in the number of radicals will significantly reduce the molecular weight of the polystyrene formed. A repeat of this experiment with the phthalate and naphthyl peroxides using no surfactant gave similar results, suggesting that the micelles do not catalyze the free radical decomposition pathway of the peroxides.

The other possible difference is that the nonaromatic cyclohexyl peroxide has differences in charge distribution and geometry leading to a different placement in the micelle. This would be a more subtle effect than the partition coefficient could show. To examine this possibilities, the geometry and charge distribution of the cyclohexane derivative and the phthalate derivative were estimated using Spartan molecular modeling software (v 5.0.3GL) using a semiempirical AM1 method. Figure 3 is the output of the computation. Hydrogens and their partial charges are omitted for clarity, so the total charges do not add up to −1 on either molecule. The charge distribution of the two peroxides, within the accuracy of the calculation method, is almost identical. The calculated distance between the first oxygen of the peroxy group and the far end of the ring is a little different, but the difference is relatively small (3.9 Å for the cyclohexyl vs 5.2 Å for the phenyl peroxide). The difference of about a single angstrom is unlikely to be significant when much larger differences, such as adding another aromatic ring or a chlorine atom, do not have much effect. These results suggest that subtle differences in charge distribution and geometric factors are probably too small to be the cause of the aberrant point. This leads to the conclusion that the amount of free radical generated is the sole reason the cyclohexyl peroxide generates a lower molecular weight polymer.

Any alternative explanation for the molecular weight trend found for these peroxides must be due to something dealing with the peroxides, as all other polymerization variables were maintained constant as well as possible. A possible explanation deals with the peroxides or their degradation products acting as radical transfer agents. Carbon tetrachloride has been used as chain transfer agents in similar systems;[46] it is possible that the halogenated aromatics could be acting similarly. Attempts to verify the chain transfer ability of these peroxides by solution polymerization failed due to solubility problems. The ionic nature of these initiators makes them poorly soluble in all but the most polar of organic solvents, which are either free radical transfer agents in their own right or free radical quenchers. However, it seems unlikely that the free radical transfer abilities would correlate so well with the partitioning abilities of the peroxides. The molecular weight of the polymer formed by the cyclohexyl peroxide (**II**) can be adjusted for the number of radicals by assuming a −0.9 power; this leads to a point that is slightly above that predicted by the other peroxides, but within the error of the measurement technique. This means that five peroxides, not all of which are halogenated and/or aromatic, would have to have radical transfer abilities highly correlated to their partitioning behavior, even though they would have to be operating by different mechanisms.

Conclusions

The octanol/water partition coefficient of the initiator has a very strong influence on the molecular weight of polymer formed, which indicates that the interface, rather than the solution, is the primary locus of polymer initiation in microemulsion polymerization. All of the polymer chains are formed from free radicals generated in the micelle itself, even with initiators that are highly water-soluble. Free radicals generated in the aqueous solvent are almost entirely lost to side reactions, in direct contrast to the mechanism of initiation proposed for similar systems. The classification of initiators as oil-soluble or water-soluble may be an oversimplification of where radicals are generated. Possibly a more nuanced description is required when describing of initiators in the context of microemulsion polymerization.

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