BOŻENA ROKITA, PIOTR ULAŃSKI*)

Technical University of Łódź
Institute of Applied Radiation Chemistry
ul. Wróblewskiego 15, 93-590 Łódź, Poland

Studies on the spatial distribution of polymeric reagents in sonochemical reactions — application of competitive kinetics**)

Summary — Intense ultrasound may initiate chemical reactions in aqueous solutions. The reactivity is not uniform in the whole sonicated volume, but rather concentrated in the close vicinity of oscillating or collapsing gas bubbles formed by the action of ultrasound (cavitation bubbles). It has been shown that certain low-molecular-weight substrates, due to their partially hydrophobic properties, tend to accumulate at the surface of cavitation bubbles, thus being particularly susceptible to ultrasound-induced chemical reactions. In this paper, using an approach based on competition kinetics method, we demonstrate that this effect takes place also in the case of polymeric substrates. Relatively hydrophobic water-soluble polymer, poly(ethylene oxide), and its oligomer poly(ethylene glycol) accumulate in the close vicinity of the bubbles. Their local concentrations in these zones may be two orders of magnitude higher than the average concentration in solution. In contrast, such effect is observed neither for strongly hydrophilic polyelectrolyte chains exemplified by poly(acrylic acid), nor for dissociated sodium acetate used as a low-molecular-weight hydrophilic model. The ultrasound-induced processes employed in the competition kinetics study in this work were the reactions of substrates with hydroxyl radicals emerging from the cavitation bubbles. In order to provide quantitative comparison with a system of uniform reactivity distribution, the same reactions were studied using ionizing radiation for OH-radicals generation.

Key words: hydrophilic polymer, hydrophobic polymer, aqueous solution, sonochemistry, competition kinetics, nonhomogeneous system, ionizing radiation, hydroxyl radicals.

MECHANISM OF ULTRASOUND-INITIATED REACTIONS

Ultrasound interacts with matter. When its energy is absorbed, the simplest effect is an increase in the absorbing body temperature. This energy, however, can initiate chemical reactions as well. Such ultrasound-initiated reactions are the subject of sonochemistry.

The basic mechanism of the reaction initiation by ultrasound in liquids can be briefly described as follows (Fig. 1). Ultrasound causes pressure variations in the liquid. When the temporary reduction of pressure falls below the threshold of tensile strength of the liquid, a rupture in the liquid occurs in a form of a small bubble filled with vapour of solvent (and possibly present gas, as well as molecules of any other volatile solutes). The formation of these bubbles and their subsequent collapse is called cavitation.

Some cavities exist only for one cycle of the sound field and collapse violently (transient cavities), while other are long-lived and oscillate around some equilibrium size (stable cavities). Cavitation is the primary effect that in consequence leads to the initiation of chemical reactions in the system. This can occur, in general, by four mechanisms (Fig. 2). Because of the high frequency of ultrasound, the implosive collapse of a bubble is an adiabatic process that leads to a rapid, momentary temperature increase to over 3000 K in the gas phase of the collapsing bubble and well above 1000 K in the thin layer of liquid adjacent to the cavity [1, 2]. If molecules of the

*) Corresponding author; e-mail: ulanskip@mitr.p.lodz.pl

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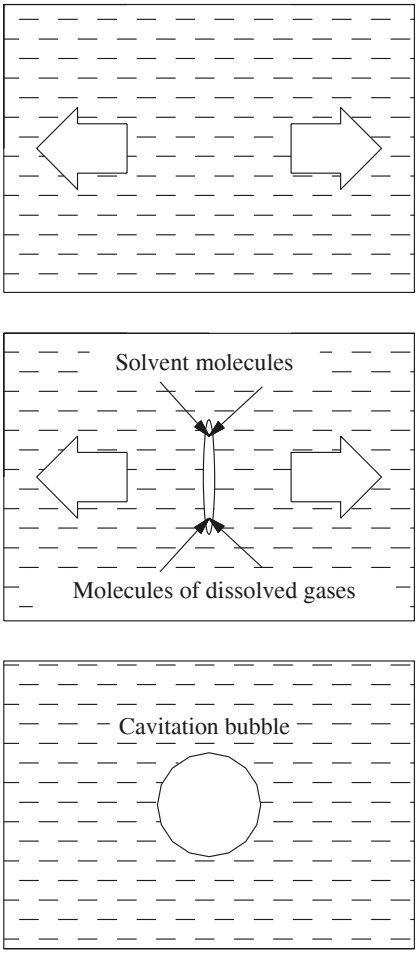


Fig. 1. Ultrasound-induced formation of cavitation bubbles, due to short-term local action of strong tensile forces on adjacent volume elements of a liquid (see text)

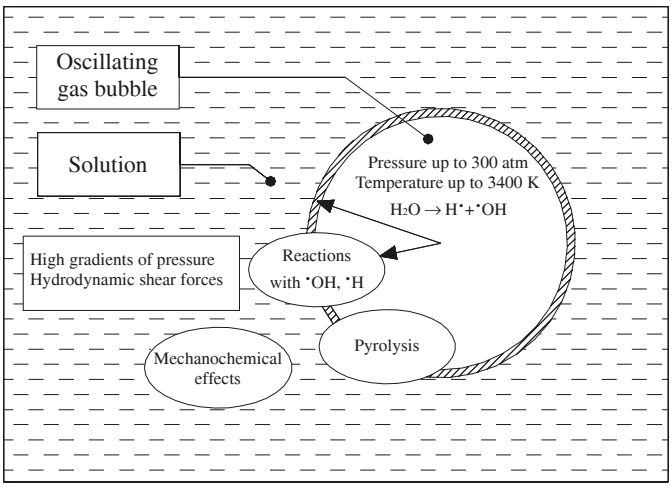


Fig. 2. Compression of a cavitation bubble in aqueous solutions, leading to chemical reactions — reaction zones and types (see text)

solute are present in the gas phase, they undergo rapid thermal decomposition (mechanism 1). Even if the solute is not volatile and is absent in the gas phase, it may still undergo pyrolysis in the hot interfacial region (mechanism 2). Solvent molecules, abundant in the collapsing bubble, may dissociate to form radicals. In case of water, hydroxyl radicals and hydrogen atoms are generated. Some of these radicals diffuse out of the cavity to the surrounding liquid, where they can react with solute molecules (mechanism 3). This mechanism makes sonochemistry similar, in a sense, to radiation chemistry, where at first solvent radicals are generated, that subsequently attack the solute (*cf. e.g.* [3]). The fourth mechanism results from the shear forces generated around collapsing cavitation bubbles. This hydrodynamic shear has no significant influence on small molecules, but is capable of breaking the chains of polymers, provided the chains are longer than a certain limiting value.

In the case of polymers subjected to ultrasound in solution, mechanisms 2, 3 and 4 are operative. Very broad evidence has been gathered for the occurrence of the shear-induced polymer degradation. Characteristic feature of this process, being in contrast with other degradation mechanisms, *e.g.* the radiation-induced chain scission, is that it proceeds in a non-random manner (breakage near the mid-point of the chain is preferred), and that there is a definite minimal chain length limiting the degradation process. When it is reached, no further chain scission is observed (for detailed discussion and a review of older data — see [4], more recent studies are reported in refs. [5—9]).

Reactivity in ultrasound-subjected cavitating liquids is, in its major part, a local phenomenon, spatially limited to the oscillating or collapsing gas bubbles (for volatile substrates) and the layer of liquid in their close vicinity (for both non-volatile or volatile substrates). Therefore, all considerations regarding kinetics and mechanisms of sonochemical reactions of non-volatile substrates, as polymers and oligomers, require precise knowledge on the local concentrations of a substrates in the reaction zone around the bubbles. This concentration may vary considerably from the average concentration of this substrate in the bulk liquid sample.

Such phenomenon has been demonstrated in aqueous solutions of low-molecular-weight organic solutes showing pronounced hydrophobic properties (e.g. surfactants) [10]. These molecules tend to accumulate at the water-gas interface, also at the surface of the cavitation bubbles, thus their local concentration in the sonochemical reaction zone may be much higher than the average concentration in solution.

In connection with our work presented in the further text it may be useful to briefly mention the main difference between experiments where hydroxyl radicals were generated by sonication and irradiation with γ-rays. Radiolysis of water and the resulting generation of OH radicals takes place uniformly in the whole volume of the system (precisely speaking, the OH concentration is uniform at the timescales of chemical reactions

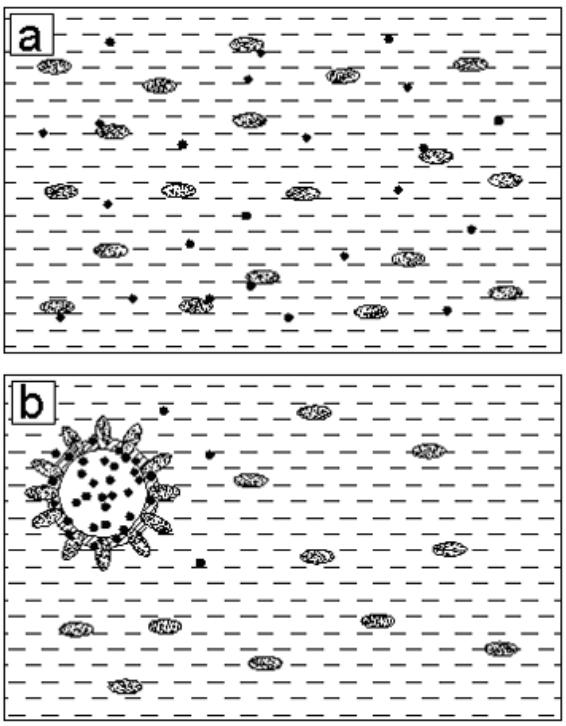


Fig. 3. Spatial distribution of hydrophobic molecules (grey ovals) in: radiation-induced (a), and ultrasound-induced (b) reactions with hydroxyl radicals (black dots) in aqueous solution; the hollow circle in scheme b) denotes the imploding cavitation bubble (see text)

with dissolved substrates). There are no cavitation bubbles that could potentially attract hydrophobic substrates to their surface. Therefore, the concentration of the substrate X in the reaction zone (*i.e.* in the whole system) is uniform and equal to its average concentration: $[X] = \overline{[X]}$ (Fig. 3a).

By contrast, in sonolysis (Fig. 3b) OH radicals are generated only at some spots — inside the cavitation bubbles — from where a part of them diffuse out to the surrounding solution. There, in a thin layer around the bubble, high concentrations of OH radicals are available for reactions with dissolved substrates. Hydrophobic substrates tend to accumulate at the surface of oscillating bubbles, and therefore their concentration in the thin layer around the bubble, which is at the same time the major OH-reaction zone, may be significantly higher than their average concentration in the whole system: $[X] > \overline{[X]}$.

IMPORTANCE AND APPLICATION OF POLYMER SONOCHEMISTRY

With this basic information in hand, one can formulate the reasons why the studies on polymer sonochemistry are considered as important and useful. First of all, they broaden our knowledge on the physical chemistry of polymers and on the sonochemical effects. Moreover, since ultrasound is nowadays widely used in medical diagnostics and therapy, it is of utmost importance to know in detail their effects on polymers, since possibly biopolymers like DNA might be affected by ultrasonic treatment. In general it has been claimed that the frequencies, intensities and application modes of the diagnostic and therapeutic ultrasound are safe, at least in the sense of free radical formation (*cf.* [11]), but some more recent experiments [12] indicate, that measurable quantities of radicals are generated under the action of therapeutic sonicators. Since also the other mechanisms mentioned above might contribute to the changes in biopolymer structure, and the amount of data on these effects is rather limited, it seems that these important questions cannot be resolved without further systematic studies on polymer sonochemistry.

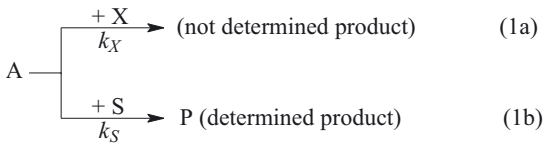
Ultrasound techniques may also constitute a powerful tool for polymer synthesis and modification. The unique property of ultrasound is that, by non-random chain scission, it can transform a polymer sample of a broad molecular weight distribution into a sample of very narrow distribution [4, 13, 14]. Preparation of such nearly monodispersed polymer samples, widely used as standards, by other techniques like fractionation is often difficult and time-consuming. A problem that is still to be solved is how to control the final molecular weight. When the underlying mechanisms are better known, one could use the mid-chain breakage feature to form block copolymers of a defined structure. Autografting and grafting reactions could also be possible.

Other applications, already being tested to some extent, are the synthesis of microspheres, disintegration of polymer aggregates, solubilization of gels and initiator-free sonochemical polymerisation [9, 15, 16]. Last but not least, one should mention that sonochemical synthesis and processing of polymers may be considered to be more environmentally friendly ("green") than many classical methods which usually involve processes performed at elevated temperature (and thus high energy consumption) and often the use of toxic initiators. To summarize, it seems that ultrasonic treatment of polymer systems has many important potential applications, but their realization and/or optimization requires more detailed basic studies on polymer sonochemistry.

DESCRIPTION OF COMPETITION KINETICS METHOD

For studying the spatial distribution of substrates undergoing the reactions with ultrasound-generated OH radicals, we applied the method of competition kinetics. This method is usually applied for a different purpose — measuring unknown rate constants that are difficult to determine directly [3, 20]. In such case, we have a substrate X of a known initial molar concentration [X] that reacts with another substrate A with an unknown rate constant k_X [reaction (1a)]. If, for any reason, direct determination of k_X is difficult or impossible, we may introduce to the system a competing substrate S, chosen such

way that the rate constant of its reaction with A (k_S) is precisely known, and the final concentration of the product of this reaction, P, can be easily measured [reaction (1b)].



Let us denote by $[P]_0$ the final concentration of P in an experiment conducted without X ([X] = 0), and by [P] the final concentration of P in another experiment where X was present at an initial concentration [X]. The ratio $[P]_0/[P]$ is related to the rate constants k_X, k_S and the initial concentrations [X], [S], by equation (2).

$$\frac{[P]_0}{[P]} = 1 + \frac{k_X}{k_S} \cdot \frac{[X]}{[S]} \qquad (2)$$

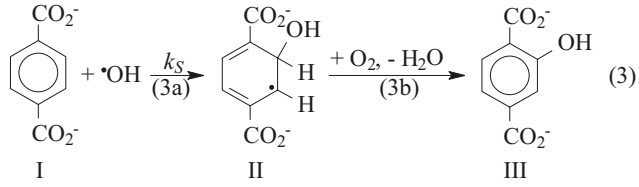
Usually, one makes a few experiments for various [X]/[S] ratios, and from the slope of the relationship corresponding to equation (2) calculates the unknown rate constant k_X.

In this work, we make use of equation (2) to determine the unknown, local concentration of a substrate X in the reaction zone of a sonochemical process — reaction with OH radicals generated in cavitation bubbles — while k_S, k_X and [S] are known.

For many low-molecular-weight organic substrates, rate constants of their reaction with OH radicals are precisely known [20]. For oligomeric and polymeric substrates, this is not the case, since the actual rate constant depends on average molecular weight and on molecular weight distribution, to name only the most important factors [21—24]. Therefore, besides sonolysis, we decided to perform parallel competition kinetics experiments using the same substrates, where OH radicals were generated by gamma radiolysis. Here the substrate distribution at the timescale of the studied reactions can be treated as homogeneous, and known, average [X] (denoted in the further text as $\overline{[X]}$), can be used to determine k_X. In fact, we were measuring the values of $[P]_0/[P] - 1$ and comparing the resulting values of right-hand side of equation (2) $[k_X \cdot [X]/(k_S \cdot [S])]$ in sonochemical and radiation-chemical experiments performed at identical nominal substrate concentrations. Since k_X, k_S and [S] are equals in both cases, the observed difference (*cf.* Fig. 6 and the corresponding discussion) must be due to the difference in [X] in the reaction zones of the sonochemical and radiation-chemical processes. In the latter process, as discussed above, the reaction zone is the whole volume of the sample and therefore $[X] = \overline{[X]}$, while in sonochemical reactions of hydrophobic molecules we expect the reaction zone to be enriched in X, thus $[X] > \overline{[X]}$ and the right-hand side of equation (2) is going to yield higher values than in the case of irradiation.

SELECTION OF THE COMPETING SCAVENGER AND EXPERIMENT CONDITIONS

An important point is to choose a proper competing scavenger S. It should fulfill the following conditions: to react with OH at a rate of similar order of magnitude as our substrates (which in all cases means diffusion-controlled rate, or nearly so), the rate constant of this reaction, k_S, should be precisely known, the spatial distribution both in sonochemical and radiolytic reactions should be uniform in the whole system, and the concentration of product P should be easy to determine. The requirement of uniform spatial distribution is easiest to fulfill by choosing a strongly hydrophilic substrate, for example an ionic substance. However, since one of our substrates, PAA oligomer, was an anionic polyelectrolyte, the competing scavenger could not bear a positive charge, to avoid any pair formation or counterion condensation effects (see *e.g.* [25]). Therefore, we have chosen to use terephthalate ions (I). This substance is often used as a dosimeter in radiation chemistry and sonochemical studies [26]. It reacts with OH radicals with $k_S = 3.3 \cdot 10^9$ dm^3 mol^{-1} s^{-1} (reaction 3a), forming initially an unstable radical (II), which in the presence of oxygen is



oxidized (reaction 3b) to yield hydroxyterephthalate (III), a stable product that can be easily quantitatively determined due to its fluorescent properties (for detailed mechanistic studies, see [26—28]).

The effectiveness of chemical changes induced in aqueous solutions by oscillation of cavitation bubbles depends, among other factors, on the nature of the dissolved gas (for detailed discussion, see [26]). The highest efficiency, measured *e.g.* as the highest yield of hydroxyl radicals, is achieved upon saturation with monoatomic noble gases, the most often used being argon. However, in the present case, saturation with argon (and, in consequence, absence of oxygen, if we neglect low-yield formation of O_2 in side reactions during sonication) would require addition of an oxidizing agent to facilitate the transformation of intermediate radicals (II) into the desired product — hydroxyterephthalate [26]. This would make the system chemically and kinetically more complex. Therefore, we decided to use air-saturated solutions, to allow oxidation of radicals (II) by dissolved oxygen.

In the reaction scheme (1a)—(1b) and in derivation of equation (2) it is assumed that no side reactions take place. In fact, during the sonochemical generation of OH

radicals their local concentrations may reach millimolar levels, and therefore their self-combination cannot be fully neglected [26]. Therefore, a small correction compensating this effect has been applied in calculations (see Appendix, *cf*. also [29]).

AIM OF THE WORK

In this paper, we present evidence that strong enrichment of the reaction zone in molecules of partially hydrophobic compound, can take place in aqueous solutions of oligomers and polymers.

In our work poly(ethylene oxide) (PEO) and its oligomer — poly(ethylene glycol) (PEG) have been selected as partially hydrophobic chains, oligomeric poly(acrylic acid) (PAA) in the ionized form was chosen as a hydrophilic macromolecule, and sodium acetate served as low-molecular-weight hydrophilic model substance. The choice of oligomeric PAA rather than high-molecular-weight material was made to avoid very high viscosity characteristic for solutions of long-chain polyelectrolytes that could possibly influence the cavitation intensity.

These substrates were tested in a reaction with OH radicals generated in aqueous solutions by the action of ultrasound and, for comparison, by the action of ionizing radiation.

EXPERIMENTAL

Materials

Materials used were as follows:

— oligomer of poly(acrylic acid) (PAA, Aldrich, nominal average molecular weight 2000 Da),

— poly(ethylene glycol) (PEG, Fluka, nominal average molecular weight 400 Da),

— poly(ethylene oxide) (PEO, Aldrich, nominal average molecular weight 200 kDa),

— sodium acetate (POCh, Poland) and sodium terephthalate (Aldrich).

All these substances were used as received.

All solutions were made up in ultrapure water (specific resistance > 18 MΩ cm, Nanopure II, Barnstead) passed through a 0.2 μm pore-size filter.

Sonication and irradiation

Solutions containing PEG and PEO were sonicated or irradiated at a neutral pH (*ca*. 6.0), while in experiments with acetate and PAA pH was set to 8.0, since dissociated forms of these substrates were required.

Sonications were performed in URS-1000 ultrasonic reactor (Allied Signal Elac-Nautik, Kiel, Germany), consisting of CESAR wave generator and amplifier, ultrasonic transducer and thermostated reaction vessel 500 mL of capacity (Fig. 4). The vibrating element of the transducer, covered with stainless steel, formed the bottom of the vessel. Ultrasound frequency was 360 kHz, the average bulk temperature of sonicated solution was 22±2 °C. The dose rate of ultrasound absorption, equal 85 W/kg, was determined by calorimetry [17]. Samples were sonicated in an open vessel, without any gas saturation.

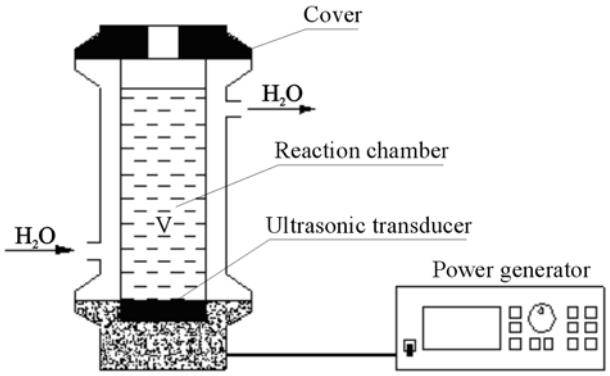


Fig. 4. Scheme of sonochemical reactor based on URS-1000 system

Gamma irradiations were performed in open 10 mL ampoules using a BK-10000 ^{60}Co source (Polon, Poland, mean energy of γ-photons: 1.25 MeV) at a dose rate of $2.50 \cdot 10^{-2}$ Gy s^{-1} as determined by Fricke dosimetry [18, 19].

Concentrations of hydroxyterephthalate, product of the reaction of hydroxyl radicals with sodium terephthalate, were determined by spectrofluorimetry (LS-4, Perkin-Elmer, excitation 315 nm, emission 425 nm).

In text below the concentrations of polymers and oligomers are given in moles of repeating units per dm^3.

RESULTS AND DISCUSSION

Enrichment of the reaction zone of sonochemical reaction in hydrophobic substrates

Aqueous solutions of terephthalate ([S] = $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3} = *const*.), pure as well as containing various average concentrations of the studied substrate, were subjected to gamma irradiation or to sonication, and the forming of the product, hydroxyterephthalate, was followed by measuring of the fluorescence intensity. Exemplary plots of competition kinetics between PEG and sodium terephthalate as the substrates are shown in Fig. 5a and 5b.

The slopes of the straight lines give the yields of the product at various nominal (*i.e.* average) substrate concentrations $\overline{[X]}$. For each substrate, the results of radiolytic and sonochemical experiments were plotted in the coordinates corresponding to equation (2), as a function of $\overline{[X]}/[S]$. In Fig. 6 the data for PEG are shown, clearly indicating a pronounced difference between the slopes obtained in radiolytic and sonolytic experiments.

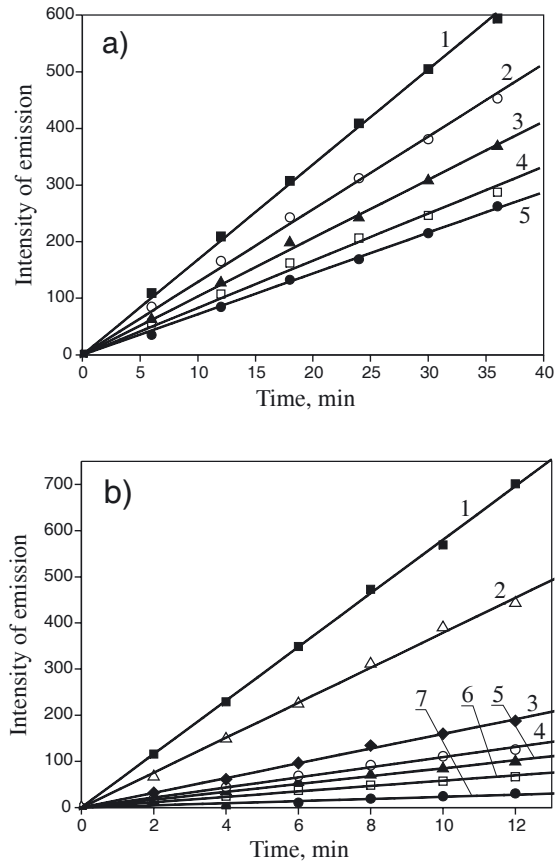


Fig. 5. Fluorescence intensity of hydroxyterephthalate (in relative units) as a function of a) irradiation time and b) sonication time for concentration of sodium terephthalate [TA] = 2 · 10^{-3} mol dm^{-3} = const. and various average PEG concentrations in 10^{-3} mol dm^{-3}: a) 1 — 0, 2 — 3.25, 3 — 6.50, 4 — 9.75, 5 — 13.0; b) 1 — 0, 2 — 0.10, 3 — 0.50, 4 — 1.00, 5 — 2.00, 6 — 6.50, 7 — 13.0

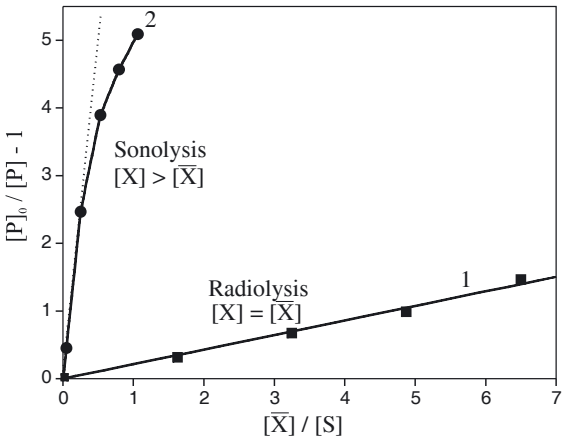


Fig. 6. Hydroxyterephthalate yield (as $[P]_0/[P] - 1$), for radiolysis (1) and sonolysis (2) of PEG with sodium terephthalate (TA) as the competing scavenger of OH radicals as a function of $\overline{[X]}/[S]$ ratio (here [S] = [TA] = 2 · 10^{-3} mol dm^{-3} = const.)

Since, as discussed before, in the case of radiolysis the X concentration in the reaction zone (whole sample volume) is equal $\overline{[X]}$, much higher slopes obtained in sonochemical experiment under otherwise identical conditions clearly indicate that the real X concentration in the reaction zone surrounding the cavitation bubbles is much higher than the average concentration of the substrate in the whole system. The enrichment factors, calculated for all substrates studied from the ratio of [X] (sonolysis) and [X] (radiolysis) = $\overline{[X]}$ at the limit of $\overline{[X]} \rightarrow 0$, are listed in Table 1.

T a b l e 1. Enrichment of the sonochemical reaction zone in the different substrate molecules, shown as approximate values of $[X]/\overline{[X]}$ for $\overline{[X]} \rightarrow 0$

Substrate	$[X]/\overline{[X]}$
CH_3COONa	1.3
PAA (M_w = 2 kDa)	2.6
PEG (M_w = 400 Da)	60
PEO (M_w = 200 kDa)	320

These data clearly illustrate the difference in sonochemical behavior of hydrophilic and hydrophobic substrates. While for acetate and ionized PAA the enrichment factor is close to 1 (*i.e.* practically speaking the concentrations of these substrates in the reaction zone and in the bulk solution are similar), more hydrophobic PEG and PEO show a strong tendency to accumulate in the reaction zone. Their local concentrations may reach values even two orders of magnitude higher than the average concentrations in the whole solution volume.

Saturation effect

One may expect that the enrichment factor defined as $[X]/\overline{[X]}$ should depend on $\overline{[X]}$, due to the limited volume of the reaction zones implying their limited capability to host the substrate molecules. With increasing average concentration of a substrate, the reaction zones become

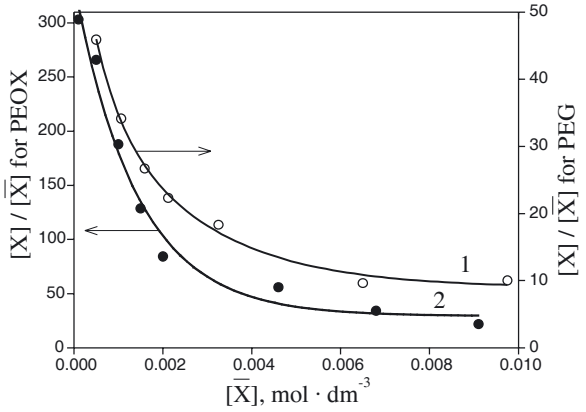


Fig. 7. Intensity of the accumulation effect of the hydrophobic substrate in the reaction zone around the cavitation bubbles as a function of the average substrate concentration: 1 — PEG, 2 — PEO

gradually saturated, and therefore the increase in [X] is slower than the rise in $\overline{[X]}$. This effect is in fact observed for both of our hydrophobic probes (Fig. 7) — the enrichment factor decreases with increasing average substrate concentration.

CONCLUSIONS

Relatively hydrophobic water-soluble polymers, when subjected to the action of ultrasound in aqueous solution, tend to accumulate at the surface of the cavitation bubbles. Since these bubbles and their close vicinity are the active zones of sonochemical reactions, hydrophobic polymers are more susceptible to ultrasound-induced reactions, *e.g.* an attack of hydroxyl radicals, than hydrophilic polymers of similar average concentration but uniform spatial distribution. This enrichment effect is particularly pronounced at low (millimolar and submillimolar) concentrations, where we have evidenced local concentrations of poly(ethylene oxide) over two orders of magnitude higher than its average concentration in solution.

Our results have also practical implications. Ultrasound is frequently used in laboratories to facilitate the solubilization of macromolecular samples, including preparation of aqueous solutions of biopolymers and synthetic polymers. Our data indicate that care must be taken when performing these procedures, especially with relatively hydrophobic polymers, since due to their high local concentrations in the sonochemical reaction zones they are especially susceptible for ultrasound-induced damage or modification (degradation, oxidation, etc.). On the other hand, partially hydrophobic water-soluble macromolecules seem to be particularly suitable for ultrasound-induced processing (*e.g.* controlled reduction of molecular weight, polymerization or probably also crosslinking), since one can expect high efficiency of sonochemical reactions even at low average concentrations of these substrates.

APPENDIX

As we have already stated previously, in derivation of equation (2) based on the reaction scheme (1a)-(1b) it was assumed that no side reactions took place. Actually, one should consider the potential influence of the recombination of OH radicals on the results obtained by this simple competition kinetics approach. The relative importance of this fast second order reaction ($k = 5.5 \cdot 10^9$ dm^3 mol^{-1} s^{-1} [20]) depends on the average steady-state concentration of hydroxyl radicals in the reaction zone. In radiolysis experiments these concentrations are very low ($<10^{-6}$ mol dm^{-3}) and OH recombination can be neglected. However, during the sonochemical generation of OH radicals their local concentrations may reach millimolar levels [26], and therefore their self-recombination and its influence on the competition kinetics experiment must be taken under consideration.

It should be stressed that in the following section, in the calculation of scavenging capacities for determination of corrected $[P]_0$, average concentrations of substrates in solution were applied ($\overline{[X]}$), therefore this procedure does not mask, or correct, the effect of increase in local concentrations of hydrophobic substrates. We only want to correct the general effect taking place both in homogeneous and non-homogeneous systems, but not the specific effect caused by non-homogeneous distribution of the reactant.

The influence of OH recombination on $[P]_0/[P]$ ratio in equation (2) would be cancelled if in both experiments (determination of $[P]_0$ and of [P]) the total scavenging capacities of the reactants, given by k_X [X] + k_S [S], were the same. In such case, always the same fraction of generated OH radicals will recombine and always the same fraction will remain available for reactions with X and S. This is, however, not the case of our experiments, since when we keep S concentration constant and increase X concentration, the total scavenging capacities of S and X increase. Therefore, a correction must be applied to compensate for these different scavenging capacities.

First, we sonicate pure sodium terephthalate solutions of various concentrations to yield a calibration curve relating the product concentration $[P]_0$ and the scavenging capacity ($[P]_0$ increases towards a limiting value corresponding to scavenging of all OH radicals at infinitely high scavenging capacity, *cf.* [26]). Now we proceed with our competition experiment, at a given total scavenging capacity k_X [X] + k_S [S], and we read from the calibration curve $[P]_0$ value corresponding to that scavenging capacity, instead of measuring $[P]_0$ at the terephthalate concentration equal [S] (*i.e.* at a scavenger capacity equal k_S [S]). This correction allows us to obtain [P] and $[P]_0$ at equal total scavenging capacities. The difference between the corrected and uncorrected $[P]_0$ values under the conditions of our study did not exceed 30 % at highest substrate concentrations.

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