Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Oskar Nuyken[a]; Klaus Meindl[a]; Alexander Wokaun[b]; Thomas Mezger[c]
[a] TU München, Lehrstuhl für Makromolekulare Stoffe, Garching, Germany [b] ETH Zürich and Paul Scherrer Institut, Villigen, CH, Switzerland [c] CRB Akzo Nobel Central Research RPB, NL, Netherlands

To cite this Article Nuyken, Oskar , Meindl, Klaus , Wokaun, Alexander and Mezger, Thomas(1995) 'A Light-Sensitive Diazosulfonate Surfactant as Emulsifier for Emulsion Polymerization', Journal of Macromolecular Science, Part A, 32: 2, 447 — 457

To link to this Article: DOI: 10.1080/10601329508019190

URL: http://dx.doi.org/10.1080/10601329508019190

MACROMOLECULAR REPORTS, A32(SUPPL. 4), 447-457 (1995)

A LIGHT-SENSITIVE DIAZOSULFONATE SURFACTANT AS EMULSIFIER FOR EMULSION POLYMERIZATION

Oskar Nuyken *), *Klaus Meindl*

TU München, Lehrstuhl für Makromolekulare Stoffe, D-85747 Garching, Germany

Alexander Wokaun

ETH Zürich and Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Thomas Mezger

CRB Akzo Nobel Central Research RPB, NL-6800 SB Arnheim, Netherlands

Abstract

A light-sensitive diazosulfonate surfactant ($Ar-N=N-SO_3^-$) was applied as emulsifier for emulsion polymerization. The resulting latex was photosensitive and coagulated during irradiation. Since photolysis of the anionic diazosulfonate surfactant in water occurs mainly via the corresponding cationic diazonium amphiphile ($Ar-N_2^+$) it is concluded that a mutually charge neutralization on the latex surface could promote coagulation during photolysis. Quantitative analysis of the diazosulfonate and of the diazonium salt during irradiation and the coagulation behavior of the latex support this view.

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*) Author to whom correspondence should be addressed

1. Introduction

Emulsion polymerization is an established technical process nowadays used for the polymerization of several important monomers such as vinylacetate, chloroprene, styrene, butadiene, and many others [1]. At least four ingredients are applied for a standard polymerization recipe: water, monomer(s), initiator and a surfactant (also referred to as emulsifier or soap). For the latter, anionic surfactants like fatty acid soaps, sulfates or sulfonates belong to the most commonly used types [2, 3].

A newer variant of emulsion polymerization employed in the last years consists in the use of destructible surfactants that can be converted to non-amphiphilic products after the polymerization has been accomplished [4, 5]. In this communication we report about the application of a photodestructible diazosulfonate surfactant ($Ar{-}N{=}N{-}SO_3^-$; structural formula shown in Fig. 1) which contains a photolabile linkage (azo bond) between the hydrophilic sulfonate group and the hydrophobic aromatic moiety.

The possibilities opened by the use of photolabile surfactants in emulsion polymerization can be delineated as follows: After polymerization has reached completion the photolabile surfactant is almost exclusively adsorbed at the surface of the latex particles, as is the case for 'normal' surfactants (see Fig. 2).

In order to destabilize the latex in a given application, the dispersion is simply exposed to UV-irradiation. The ionic headgroup of the surfactant is thereby split off by photolysis, and the latex particles aggregate (coagulate) as displayed in Fig. 2.

It has been stated [6] that photolabile latices could be useful for latex applications such as coatings, where ionic species as the charged surfactant head group are undesirable, as they might deteriorate the water resistance of the resultant polymer film.

2. Results and discussion

2.1. Photolysis of diazosulfonate surfactants

Diazosulfonate surfactants ($Ar{-}N{=}N{-}SO_3^-$; Ar: alkylsubstituted aromatic moiety) are representatives of photolabile surfactants, and have been the subject of several recent

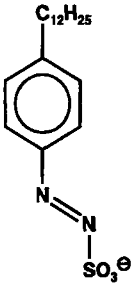

Fig. 1: Structure of the diazosulfonate surfactant C12 used for emulsion polymerization

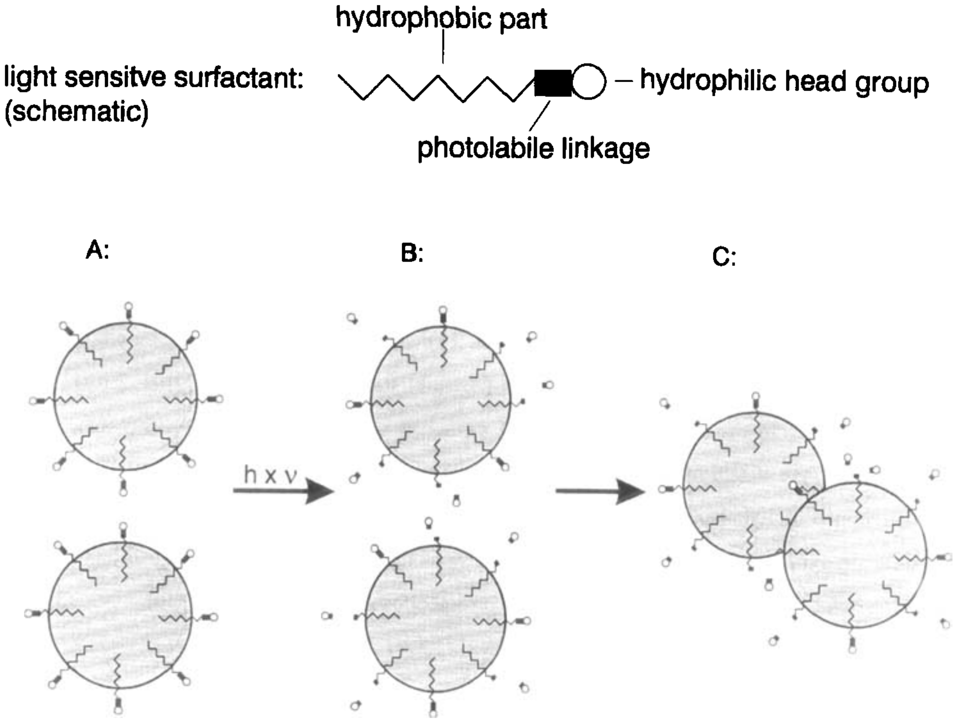

Fig. 2: Use of photolabile surfactants in emulsion polymerization. **A**: latex particles, stabilized with light-sensitive surfactants before irradiation (schematic); **B**: latex particles during irradiation; the ionic surfactant head group is split off or destroyed; **C**: coagulation.

publications [6-9]. These compounds may be photochemically cleaved in water to yield a sulfite ion and the corresponding diazonium compound, which is further photolysed in a second step. Among the different para-substituted diazosulfonate amphiphiles investigated in our groups (see ref. [7-9]), the surfactant sodium 4-dodecylphenyldiazosulfonate (abbreviated as **C12**, according to the carbon atoms in the alkyl chain; see Fig. 1) was selected for emulsion polymerization, in view of its structural similarity to the commonly used (photostable) surfactant sodium 4-dodecylphenylsulfonate. The pathway of aqueous photolysis [7] of the diazosulfonate surfactant **C6** (sodium 4-hexylphenyldiazosulfonate), which differs from **C12** only by the alkyl chain length, is illustrated in Fig. 3. In dilute solutions ($c \sim 1 \cdot 10^{-4}$ mole/l) photolysis occurs via the corresponding diazonium compound to yield an uncharged product, mainly to the corresponding phenol. In more concentrated solutions ($c \sim 1 \cdot 10^{-2}$ mole/l) this process is accompanied by precipitation of a diazosulfonate/diazonium salt complex (for further details, cf. the discussion in [7]).

2.2. Investigated latices

Two latices were prepared by emulsion polymerization of MMA (methyl methacrylate) according to the procedures summarized in Table 1. The light-sensitive diazosulfonate surfactant **C12** was used as emulsifier for latex **1** (the latex exhibited yellow colouration caused by the diazosulfonate UV absorption ($\lambda_{max.}$= 306 nm)). A reference latex **2** was synthesized with the common (photostable) surfactant sodium 4-dodecylphenylsulfonate instead of the diazosulfonate surfactant. The mean particle sizes of both latices were determined by light-scattering methods and were found to lie within the same range. The radii of gyration R_g of latex **1** and latex **2** were determined as 24 nm and 29 nm, respectively, and the hydrodynamic radii R_h corresponded to 41 nm and 44 nm [10].

2.3. Photolysis experiments concerning the latices

A diluted sample of latex **1** was irradiated in a quartz cuvette (thickness: 1 mm) with the UV-light of a xenon high-pressure lamp. The sample was diluted with distilled water (1:4 by volume) in order to restrain scattering from the latex particles, and to achieve a high photolysis rate. After a short time of irradiation (~1 minute) an incipient turbidity of the

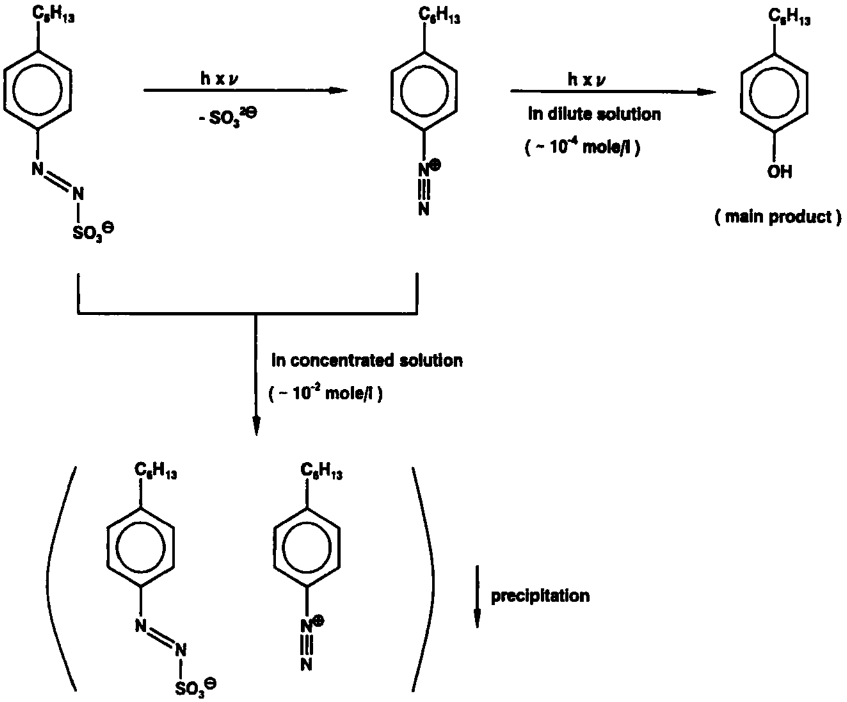

Fig. 3: Photolysis of the diazosulfonate surfactant **C6** (sodium 4-hexylphenyl-diazosulfonate) dissolved in water (from [7]).

Tab. 1: Preparation parameters for the light-sensitive latex **1** and photostable latex **2**.

Polymerization time: 6 h; temperature: 60 °C; MMA: methyl methacrylate.

	surfactant	**monomer**	**water (deionized)**	**initiator**
latex 1 **(photosensitive)**	0.470 g ($1.25 \cdot 10^{-3}$ mole) sodium 4-dodecylphenyl-diazosulfonate	25 g MMA	200 g	0.067 g $K_2S_2O_8$
latex 2 **(photostable)**	0.435 g ($1.25 \cdot 10^{-3}$ mole) sodium 4-dodecylphenyl-sulfonate	25 g MMA	200 g	0.067 g $K_2S_2O_8$

previously transparent latex layer indicated that coagulation of the latex particles had started. In contrast to this behaviour, a diluted sample of the reference latex **2** (prepared with the photostable surfactant 4-dodecylphenylsulfonate) did not exhibit any turbidity when irradiated for about 15 minutes under the same conditions.

Another photolysis experiment was carried out to investigate the significance of the diazonium surfactant, which is an intermediate of the photolysis process (cf. Fig. 3), for the coagulation process.

As the diazonium amphiphile is oppositely charged as the anionic diazosulfonate surfactant, a mutual charge neutralization on the latex surface might diminish the effective negative charge and hence promote aggregation of the latex particles. In order to investigate this point an undiluted sample of latex **1** (continuously stirred) was irradiated in a quartz beaker with the xenon high-pressure lamp. An intraphotometer was immersed into the latex to detect any change in turbidity during irradiation. The intraphotometer is based onto an emitter and a detector fiber bundle; when coagulation started the detected light intensity was weakened by the coagulated latex. The relative concentrations of the diazosulfonate and diazonium surfactant in the latex were determined by separate UV-measurements. A plot of these quantities as a function of irradiation time is shown in Fig. 4.

From the turbidity curve of the intraphotometer, which is included in Fig. 4, it is clear that coagulation occurs in the same time range where the diazonium concentration passed through a maximum, and where only a small excess of effective negative surfactant charge (about 10 % - 20% of the initial amount) was still present.

Under the assumption that the measured concentration values are representative for surfactants on the latex surface (which would hold true if both surfactants were completely adsorbed at the latex particles), it is reasonable to assume that mutual charge neutralization was promoting coagulation in the examined case. Of course, the final loss of surface charge by total photolysis of the diazosulfonate surfactant leading to an uncharged product would also induce coagulation. Whether or not charge compensation is important for coagulation

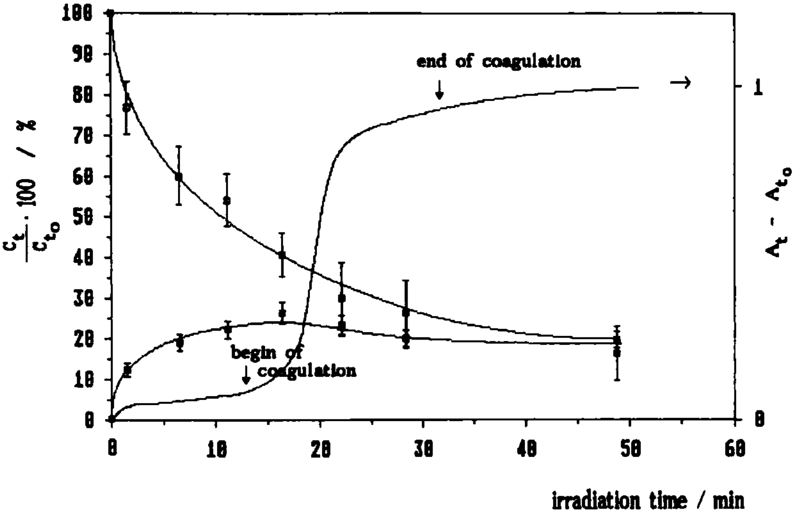

Fig. 4: Irradiation of latex 1 with a xenon UV lamp.

□ : percentage of the diazosulfonate surfactant C12 in the latex (with error bars) relative to the initial surfactant quantity.

■ : percentage of the corresponding diazonium surfactant in the latex (with error bars) relative to the initial surfactant quantity.

Relative turbidity values recorded by the intraphotometer are displayed on the right ordinate scale

A_t: logarithm of intensity detected;

A_{t0}: logarithm of intensity measured prior to photolysis;

$A_{50\,min}$: logarithm of intensity after 50 min photolysis

will depend on the relative rates of photolysis and aggregation, and might be different depending on the particular surfactant chosen. In the case of slow coagulation, one might imagine an intermediate stage of photolysis in which the latex was stabilized by positively charged diazonium groups. Zeta-potential measurement performed at various stages of the photolysis might be helpful to further clarify this effect.

3. Experimental section

3.1. Preparation of the latices

The emulsion polymerization and all procedures to be described were performed in an argon atmosphere to exclude the presence of oxygen. A mixture of 150 g of deionized water and 25 g of MMA (methyl methacrylate) was stirred in a Büchi lab autoclave thermostated at 60°C (reactor volume: 250 ml; stirring speed: 600 rpm)). In the case of latex **1** (see Table 1) the reactor was wrapped with aluminium foil to darken the reaction vessel. A quantity of 50 g deionized water containing the appropriate amount of surfactant (0.470 g sodium 4-dodecylphenyldiazosulfonate for preparation of latex **1**, or 0.435 g sodium 4-dodecylphenylsulfonate respectively for preparation of latex **2**; see Table 1) were warmed up to about 67°C in a separate darkened glass flask. In the course of this procedure the surfactant gradually dissolved. At this point 0.067 g potassium persulfate were added to this solution. After short stirring the surfactant/initiator solution was transferred into the reactor. Even after the addition of the diazosulfonate surfactant the MMA/water emulsion was only stable when stirred. In a polymerization time of 6 hours at a temperature of 60°C, a conversion of 98 % ±2 % was reached. Immediately after preparation the latex was cooled to room temperature, and filtered in air. The amount of coagulate was less than 2 % in both cases. The photolysis experiments were performed on the day following the preparation procedure.

3.2. Chemicals

Methyl methacrylate was purified from the inhibitor by passing through a basic aluminium oxide column. The monomer was distilled in vacuo and stored under an argon atmosphere. The water used for emulsion polymerization was deionized and purified by passing through a Milli-Q Ultra-Pure water system (Millipore company). Subsequently, the solvent was degassed by distillation in vacuo to remove dissolved oxygen, and also stored under an argon atmosphere. Potassium persulfate, used as the initiator, was obtained from Fluka in puriss. p. a. quality.

For synthesis of the diazosulfonate surfactant **C12**, 4-dodecylaniline was diazotised with sodium nitrite in acidified water. The diazonium salt produced by this step was coupled with sulfite in an alkaline buffered solution. The synthesis has been described in detail in [7]. The surfactant sodium 4-dodecylphenylsulfonate was prepared according to reference [11].

3.3. Photolysis experiments

Photolysis experiments were performed with a 150 W Xenon high-pressure lamp. To avoid heating of the irradiated samples, the light was passed through an IR water filter. Diluted samples of latex **1** and latex **2** were irradiated in a quartz cuvette (Hellma) with a thickness of 1 mm and were shaken thereafter. The experiment for the determination of the diazosulfonate and diazonium concentration as a function of irradiation time (see section 2.3.) was carried out in a quartz beaker (diameter: 4.5 cm) containing. ~ 65 g of undiluted latex **1** which was stirred during irradiation. The determination of the concentrations itself is described in section 3.4. At the end of the coagulation process, the precipitated polymer was filtered off by a fine-porous filter. In all photolysis experiments the distance of the irradiated samples to the xenon lamp was about 60 cm.

3.4. Determination of the diazosulfonate and diazonium concentration

During irradiation of latex **1** in the quartz beaker aliquots of ~ 1.6 g were taken with a pipette after different irradiation times, and immediately injected into 95 ml of distilled THF, which had been acidified with about 0.45 g of a 1 wt. % hydrochloric acid. Acidification prevents the reverse reaction of the photochemically generated diazonium compound with sulfite ions reforming the diazosulfonate; this reaction does not take place with hydrogensulfite ions (HSO_3^-) [7]. Thereafter, the THF solution was filled up with THF to exactly 100 ml, and was strongly shaken for about one minute to dissolve precipitated polymer. The determination of the diazosulfonate and diazonium concentrations of these samples is outlined below:

About 10 ml of this parent solution were separated for recording of an UV spectrum. The UV spectrum was recorded within 3 minutes after the preparation of the parent solution to avoid decomposition of the diazonium compound. In the wavelength range between 260 and 320 nm, the UV spectrum represented a superposition of the diazosulfonate ($\lambda_{max.}$= 287 nm, ε = 13200 $l \cdot mole^{-1} \cdot cm^{-1}$) and diazonium ion absorptions ($\lambda_{max.}$= 276 nm, ε =

14300 l · mole^{-1}· cm^{-1}; values given refer to a solution in THF containing about 1-2 % of water).

To resolve the recorded UV spectrum into the individual contributions, the diazonium concentration was determined separately by azo coupling. For this purpose, the remainder of the parent solution (about 90 ml) was mixed with 1 g of a 0.72 wt. % hydrous 1,3-diaminobenzene solution. The diazonium concentration could be determined from the UV spectrum of the formed azo dye (2′,4′-diamino-4-dodecyl-azobenzene; the added amount of the 1,3-diaminobenzene corresponded to a 35 fold excess on average, relative to the diazonium compound).

The diazonium contribution to the UV spectrum was then calculated from the determined concentration, and subtracted from the parent UV spectrum to yield the diazosulfonate spectrum. From the latter, the diazosulfonate concentration was calculated.

During the measurements and procedures described above, daylight was excluded (e. g. the vessels of the parent solutions were be wrapped with aluminium foil) to prevent photochemical decomposition of both the diazosulfonate and diazonium surfactant.

Acknowledgment

The authors should like to thank M. Schmidt and M. Mirke (Universität Bayreuth) for performing the light scattering measurements on latex **1** and **2** (ref. [10]). Financial support of this work by Akzo Nobel company is greatfully acknowledged.

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