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Photosensitive 2,5-distyrylpyrazine particles produced from rapid expansion of supercritical solutions

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Abstract

Solvent-free, photoreactive particles of 2,5-distyrylpyrazine (DSP) monomer were developed by rapid precipitation from an expanding supercritical chlorodifluoromethane solution. DSP polymer particles were produced by solid-state photopolymerization. DSP particles below a critical diameter of about 0.5 μm were found to be mechanically stable and did not fragment upon photopolymerization. The rate of DSP photopolymerization was shown to be size-sensitive. Nano-scale particles demonstrated superior photoreactivity in the solid state in comparison to micro-scale crystals. UV spectra of DSP at different degrees of conversion were investigated and the extinction coefficients were calculated for the DSP monomer and polymer in sulfuric acid.

Keywords: 2,5-Distyrylpyrazine; Solid-state polymerization; Supercritical

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1. Introduction

The solid-state polymerization of 2,5-distyrylpyrazine (DSP), reported in 1958 [1] and reintroduced later in 1967 by Hasegawa [2], is a classical example of topochemical polymerization. DSP polymerization was extensively studied, but the resultant polymer has found limited practical applications, primarily because of substantial mechanical disintegration or cracking of the crystal upon polymerization. However, very small DSP monomer particles, which could change properties upon exposure to light or chemicals without undergoing fragmentation might be useful in various applications such as optical data storage and chemical sensing.

The solid-state polymerization of DSP is a four-center polymerization reaction, and is depicted in Fig. 1 [3,4]. The reaction proceeds upon irradiation by UV [1,3–6] and visible light [3–6] and does not require the use of external photoinitiators. The degree of polymerization depends on the wavelength of the exciting light and wavelengths shorter than 400 nm are needed to obtain high molecular weight DSP polymer [7]. The crystal structure of the monomer plays an important role in the reaction, as the polymerization goes by direct rearrangement of molecules from the monomer to the polymer without diffusion [4]. The change in the lattice spacing due to the molecular rearrangement produces stress within the crystal, which form cracks propagating along the chain growth directions [4]. As a result, the polymer crystal disintegrates into rod-like fragments. Homogeneous polymerization has been suggested as a possible way to avoid the mechanical disintegration [8,9] and has been reported by irradiation at wavelengths longer than 400 nm [6,10]. Unfortunately, as was pointed out earlier, the polymerization reaction in DSP is incomplete at these longer wavelengths [8,10]. However, because the lattice is less constrained in small-diameter particles with a high surface-to-volume ratio, it seems reasonable to assume that small DSP particles below a critical diameter can be polymerized at shorter excitation wavelengths without fragmentation. However, to the best of our knowledge, no work has been published on the development and properties of submicron DSP crystals, possible due to the difficulty in obtaining submicron DSP monomer particles.

In this work, small DSP particles were produced using the technique known as Rapid Expansion of Supercritical Solutions (RESS). Small organic particles have been described in the literature, including microcrystals from materials with solid-state polymerization [11]. The particles

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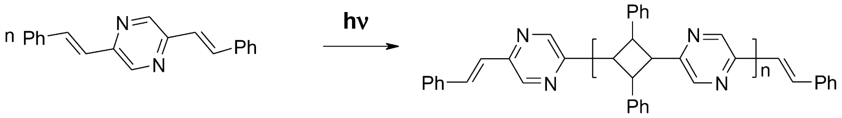


Fig. 1. Schematic of DSP polymerization reaction.

are normally produced in liquid solvents and the monomer crystals are usually polymerized immediately after formation while still dispersed in the solution. However, for some applications, dry process data storage materials for example; it is beneficial to have reactive monomer particles in the final product that can be polymerized at a later time. Our previous results demonstrated that small, solvent-free particles, including DSP monomer, can be produced using RESS [12,13].

RESS is based on the sudden change in a solute solubility and solvent density upon the rapid decompression of supercritical solution through an expansion device, such as an orifice or capillary nozzle [14]. In general, the precipitates have a narrow and tunable size distribution with mean size ranging from nanometers to micrometers [15–17]. The solvent becomes a gas after the expansion and separates from the solute, leaving behind dry solute particles. The phase separation takes place at a time scale determined by the local speed of sound and the geometry of the expansion device. Therefore, it is possible to develop particles with non-equilibrium properties [18]. In this paper we describe the development and analysis of small (submicron) DSP monomer particles produced from a rapidly expanding supercritical solution.

2. Experimental

2.1. Particle development

The DSP monomer was synthesized by the method of Hasegawa et al. [3] and recrystallized from toluene. The monomer purity was checked by TLC chromatography. The melting point of the DSP monomer was measured to be 223 ± 1 °C (toluene). Chlorodifluoromethane was from DuPont and used as supercritical solvent. The solubility and phase behavior of DSP in supercritical chlorodifluoromethane was measured using a high-pressure view cell [13]. The phase separation was visually observed and defined here as the pressure at which the first crystals appeared upon isothermal depressurization. Small DSP monomer particles were developed using the RESS apparatus, consisting of an extraction vessel coupled to a capillary nozzle with a 100 μm inner diameter, described previously [13]. UV and visible light below 610 nm was filtered to prevent monomer polymerization during the experiment. The RESS precipitates and other particles were examined by SEM (LEO 1530 VP), AFM (Digital Instruments, NanoScope IIIa) and optical microscopy.

2.2. Photopolymerization

A 100 Watt UV mercury lamp providing a broad spectral output down to approximately 254 nm (PC-100S, American Ultraviolet Co) was used for the photopolymerization of the DSP samples. The source-to-sample distance was approximately 22 cm, unless otherwise noted. The UV lamp used was a medium pressure, metal halide lamp-Type D, Iron-doped. The spectral irradiance at wavelengths of 228–420 nm was 420,000 microwatts/cm^2 with the irradiance at the maximum (365 nm) of 23,000 microwatts/cm^2 according to the manufacturer. As mentioned above the degree of polymerization in DSP depends on a variety of factors such as the excitation wavelength, the exposure time and the temperature. The UV lamp emits excitation wavelengths short enough to achieve a high degree of polymerization in DSP. However, for reference, a cut off filter transmitting wavelengths longer than 435 nm (GG-435 from Melles Griot) was used to produce the oligomer form described in the literature.

2.3. UV spectroscopic analysis

A UV spectroscopic study was performed using a spectrophotometer (Perkin Elmer model Lambda 40). Concentrated (95%) sulfuric acid was used as a common solvent for all forms of DSP. UV reference spectra were taken from monomer, polymer and oligomer forms of DSP prepared according to recipes provided in the literature. The DSP monomer reference solution was prepared by dissolving the originally synthesized crystals in sulfuric acid under dark conditions. The DSP polymer for the reference spectra was prepared similarly as described by Hasegawa [3]. Original monomer crystals (100 mg) were dispersed in 4 ml of hexane and, while stirring, were irradiated using a 100 Watt UV lamp for 8 h at room temperature until the color had changed from yellow to white. The resultant polymer was then washed with acetone and hexane, filtered, and vacuum dried. The oligomer form for the reference spectra was prepared as described in Ref. [5]. The monomer DSP was first recrystallized from benzene. After slow benzene evaporation in a dark environment, DSP crystals were formed and adhered to the glass surface. The oligomer form was developed by irradiation of the crystals with a 100 Watt UV lamp for 1 h through a cutoff filter transmitting wavelengths longer than 435 nm.

Small DSP monomer particles produced from RESS were deposited directly onto microscope slides and irradiated for 1 min by the UV lamp and then dissolved in sulfuric acid.

2.4. X-ray analysis

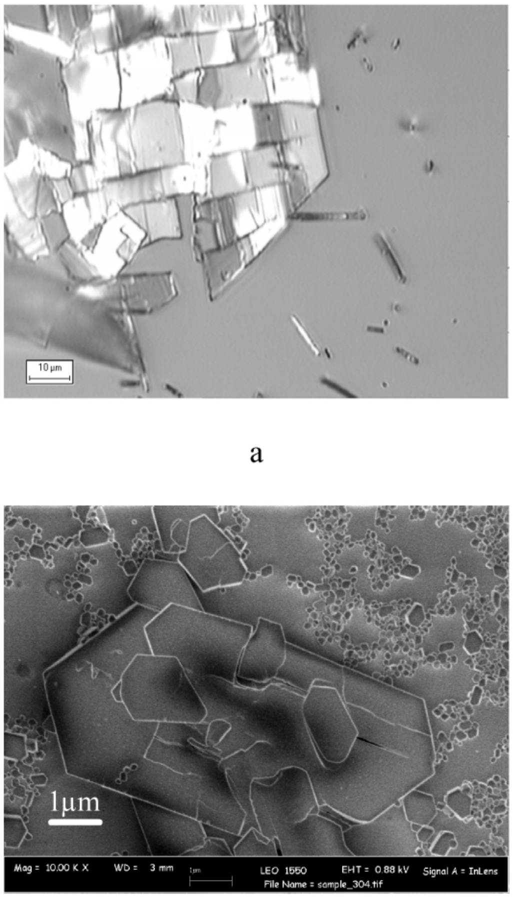
An X-ray study was conducted using a Phillips, X'Pert MRD diffractometer, in phase analysis mode. Reference diffraction patterns for the monomer, oligomer and polymer forms of DSP were obtained from crystals recrystallized from benzene as described in Ref. [5]. After slow benzene evaporation in a dark environment, DSP crystals were formed and adhered to the glass surface. The polymer sample was developed by irradiation of the crystals with a 100 Watt UV lamp for 1 h. Oligomer DSP was developed similarly, but irradiated through a cutoff filter.

Small DSP particles from RESS were directly sprayed onto a glass microscope slide and X-ray data was obtained for both the monomer and polymer forms for comparison to the reference.

3. Results and discussion

3.1. Critical size estimation

Stress release during the photopolymerization of DSP results in the formation of large cracks in the directions of chain growth, which is parallel to the *c*-axis of the monomer crystal [4]. Literature data [4,7] and our own SEM and OM images were used to estimate the critical size, defined here as the dimension of the smallest DSP fragment produced during polymerization. Optical and SEM photographs of the DSP crystals after UV irradiation are shown in Fig. 2. The optical image (Fig. 2a) shows a partially polymerized crystal containing a large number of cracks as well as small separate fragments. By carefully analyzing the fragmentation products using both OM and SEM (Fig. 2b), we estimate that the critical dimension is on the order of 0.5–1.0 μm. Therefore, our goal was to develop DSP monomer particles below 0.5 μm in diameter and to investigate their mechanical stability during polymerization. RESS appeared to be a suitable technique to create particles in this size range.



a

b

Fig. 2. Fragmentation of DSP crystal during polymerization.

3.2. Particle development

No data was found on the solubility of the DSP monomer in supercritical chlorodifluoromethane. Therefore, the phase behavior was measured and is reported here in Fig. 3. Each data point represents the mean between 3 experiments at the same temperature. IR spectra showed no difference in chemical structure of the initial DSP monomer and the monomer recovered after being subjected to supercritical chlorodifluoromethane at temperature up to 135 °C and pressure up to 620 bars. There also was no visible change in the yellow color of the precipitated DSP compared to the initial DSP monomer. Therefore, DSP monomer was found to be stable in chlorodifluoromethane at the conditions studied. The resultant phase separation curve was used for optimization of the RESS parameters as described in Ref. [13]. The RESS conditions favoring the formation of small DSP particles ranging in size from 100 to 300 nm are: DSP concentration 0.15 wt%, preexpansion pressure and temperature 345 bars and 125 °C. The small particles were deposited directly onto surfaces of interest, such as microscope slides or SEM stubs, for further analysis. The particles were found to be free of solvent, as supercritical chlorodifluoromethane turned into a gas under atmospheric pressure and room temperature and evaporated instantly.

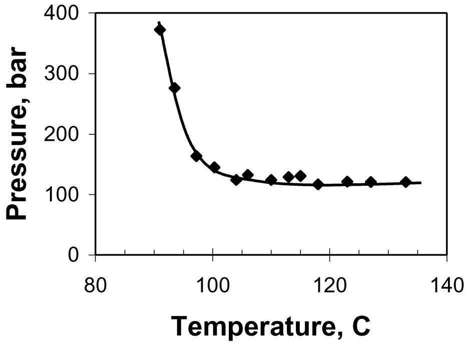
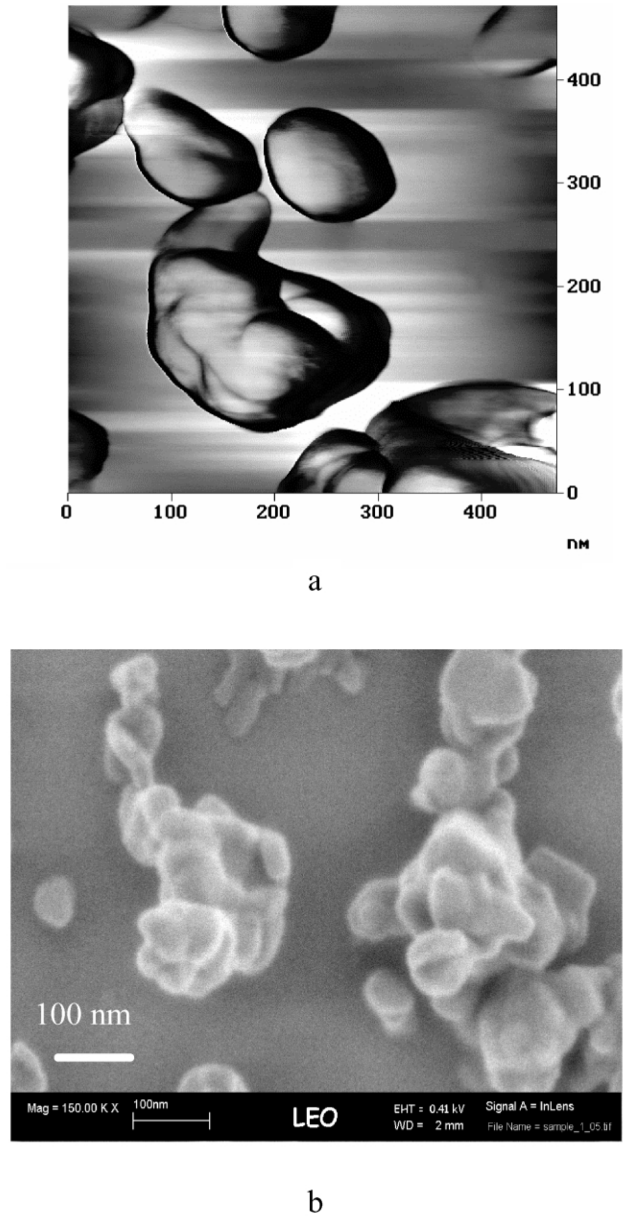


Fig. 3. Solubility of DSP (0.15 wt%) in supercritical chlorodifluoromethane.

Fig. 4 is an AFM phase image of DSP particles developed by RESS and irradiated by UV light for 10 min. All of the particles are smaller than 0.5 μm and the typical diameter ranged from 0.1 to 0.3 μm. AFM images taken before and after polymerization revealed that the general shape and size of the particles did not change during polymerization. The nanoparticles initially exhibited the same yellow color as the original DSP crystals but they became white under UV or sunlight exposure for several minutes indicating a high degree of photoreactivity. The rounded shape of the particles suggests that the particles formed by RESS exhibited a lower degree of crystallinity in comparison to the original highly crystalline monomer material.



a

b

Fig. 4. AFM phase image (a) and SEM image (b) of small DSP polymer particles developed by rapid expansion of supercritical chlorodifluoromethane and after UV irradiation.

3.3. Structure analysis

X-ray data for DSP crystals has been disclosed in the literature, but only for the powder method and not for small particles. We used the phase analysis mode to study the relative crystallinity of the small DSP particles. First, diffraction patterns were obtained for reference DSP crystals developed according to the method described above. The resulting X-ray data, shown in Fig. 5a–c, was used here as a reference for comparison with diffraction patterns of the small particles produced from RESS. No diffraction peaks were observed for the small DSP particles produced from RESS and polymerized by UV light (Fig. 5d). The absence of diffraction peaks along with the rounded particle geometry observed in the AFM analysis suggests that particles are not highly crystalline. Amorphous DSP powder was developed previously only by polymerization in solution when irradiated at 380 nm [7]. The amorphous state is a non-equilibrium form of DSP; therefore, amorphous particles are expected to eventually recrystallize and we found that the recrystallization process can be accelerated in these DSP particles by exposure to vapors such as (−)-methyl L-lactate vapor. After vapor treatment and UV irradiation, diffraction peaks appeared in X-ray spectra (Fig. 5e), similar to those for the reference polymer developed from the benzene-recrystallized crystals (Fig. 5c). The shape of the particles also changed from a rounded, spherical geometry to a more crystal-like structure (Fig. 6a,b).

The fact that small, largely amorphous DSP particles can undergo photopolymerization in the solid state was somewhat unexpected. It was expected that, for the topochemical reaction to proceed, the centers of molecules should be in close proximity. For example, it was previously reported that amorphous diacetylene particles dispersed in solution

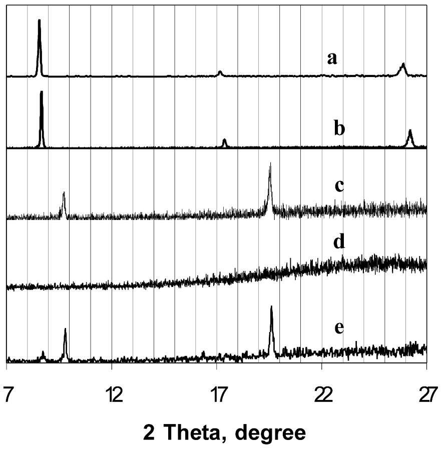
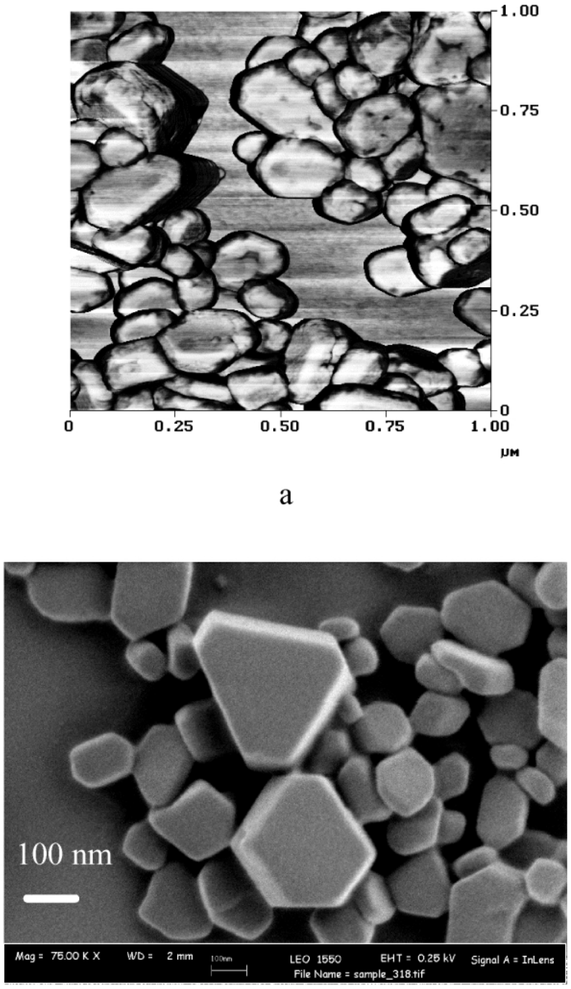


Fig. 5. X-ray diffraction data of DSP monomer (a), oligomer (b), polymer (c), crystals and small particles developed by RESS and polymerized immediately (d) and after recrystallization (e).



a

b

Fig. 6. DSP polymer particles developed from supercritical chlorodifluoromethane, recrystallized by vapor treatment and polymerized by UV light. (a) AFM phase image; (b) SEM image.

were not able to polymerize [11]. It is possible that the X-ray analysis was not sensitive enough to reveal regions of crystallinity in these very small DSP particles and additional data is required for a complete understanding of this effect, but this is beyond the scope of the present study.

3.4. Polymerization and photoreactivity

As can be seen from Figs. 4 and 6, there is no visible fragmentation or cracking developed in the small amorphous or semicrystalline DSP particles after photopolymerization. This supports the earlier assumption that particles below the critical dimension can accommodate the internal stress state produced by the polymerization process. The X-ray data suggests that the more crystalline particles (Fig. 5e) have patterns similar to the polymer, not oligomer form of DSP.

In order to estimate the degree of polymerization in the DSP particles, UV–Vis spectroscopy in solution was performed. UV–Vis spectroscopy has been previously used for DSP analysis at different degrees of conversion, both in the solid state and in solution [6,7]. The absorption bands for DSP in solution are different from the absorption bands in the solid state. It was found that the DSP monomer, oligomer and polymer structures exhibit UV–Vis absorbance in different wavelength regions, both in the solid state and in solution. This was expected from the physics of the 2 + 2 cycloaddition reaction in DSP and is due to the three distinct chromophors for DSP, each dominated at a different degree of conversion. In the monomer form of DSP there is only distyrylpyrazine unit, which can be assigned to a strong distyrylpyrazine absorbing chromophore. In the oligomer form, which is mainly a pentamer, according to the literature [7], there are styrylpyrazine end groups and pyrazine groups (chromophors). The polymer form is dominated by the pyrazine with a negligible amount of styrylpyrazine chromophors. Unfortunately, the quality of the data published for different solvents was unsatisfying and we searched for a more suitable solvent for this evaluation. Concentrated sulfuric acid was selected because of its excellent spectroscopic properties with no absorbance in the DSP absorbance region. Also DSP should be in the protonated form in the sulfuric acid solution because of the nitrogen in the pyrazine ring. UV spectra of DSP monomer, polymer, and oligomer in sulfuric acid are presented in Fig. 7. As can be seen, no base line distortion is present indicating the absence of clustering (turbidity effect). The polymer absorbance peak is also fully resolved. The extinction coefficients were calculated for the DSP solutions. Monomer DSP in sulfuric acid exhibits two absorption peaks centered at 588 nm ($\varepsilon = 3.52 \times 10^4 \times$ *L/cm mol*). and 404 nm ($\varepsilon = 3.11 \times 10^4$ *L/cm mol*). Polymer DSP exhibits one absorption peak at 324 nm ($\varepsilon = 1.23 \times 10^4$ *L/cm mol*). The oligomer DSP exhibits two absorption peaks at 511 and 361 nm. Therefore, it is possible to estimate the degree of conversion of the DSP particles by UV–Vis spectroscopy in concentrated sulfuric acid solution.

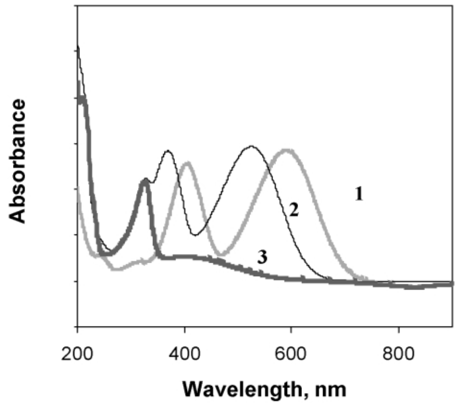


Fig. 7. UV spectra of DSP monomer (1), oligomer (2), polymer (3) crystals in concentrated sulfuric acid.

Fig. 8 represents the UV spectra of both the nano-scale and micro-scale crystals irradiated for 1 min by the UV lamp and dissolved in concentrated sulfuric acid. From this data it is clear that the DSP nanoparticles exhibit a very high degree of polymerization after 1 min of irradiation. No oligomer peak is present under the conditions studied. The analysis of the number of molecules converted is needed to compare the reaction rate in nano and micro crystals of DSP, but this is beyond the scope of this investigation.

Interestingly, the micro-scale crystals remained primarily in the monomer form with little polymerization, as indicated by the dominance of the absorption peak at 324 nm (Fig. 8(1)). This data supports the earlier observation that the rate of polymerization in the nano-scale mono DSP particles produced from RESS is significantly greater than the larger DSP crystals. Although the photopolymerization of DSP crystals has been previously studied by IR [4], Raman [19], UV [6,19] spectroscopy, X-ray diffraction [4–6], and AFM [20], we found no information on the formation or polymerization of small-scale DSP particles. On the other hand, size-dependent polymerization rates have been reported for several materials with solid-state reactivity, such as cinnamic acid and derivatives [20] and diacetylenes [21]. However, nano-scale diacetylene microcrystals, for example, exhibited a lower photoreactivity than micro-scale crystals [21].

The reason for the enhanced photoreactivity of the nano-scale particles is not completely clear at this time. One possible explanation is the increase in the surface to volume ratio. If the photopolymerization reaction is initiated from the surface, as was proposed previously [5,7], and the polymerization rate of DSP depends on the light intensity [5], small particles would be expected to have enhanced reaction rates because the intensity of the transmitted light can be significantly attenuated in the interior of a large crystal. Another possible explanation is the stress distribution within the particle during photopolymerization. In large crystals partial polymerization creates an unbalanced stress distribution throughout the crystal volume and, as a result, cracks are formed. However, the role of physical disintegration on the photopolymerization rate was not investigated.

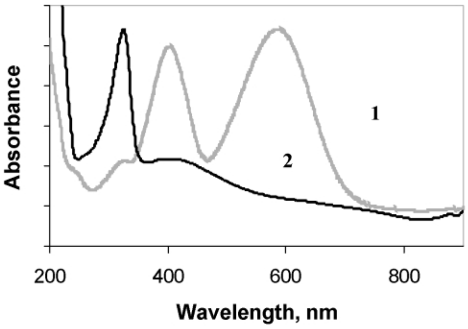


Fig. 8. UV spectra of DSP microcrystals (1) and DSP small particles developed by RESS (2) irradiated for 1 min then dissolved in sulfuric acid.

It is possible to estimate the particle size, below which the DSP can be considered optically thin. Assuming, for simplicity, isotropic light absorbance by the DSP crystals and estimating that the molar extinction coefficient for solid DSP is on the order of ($\varepsilon \approx 10^4\ L\,mol^{-1}\ cm^{-1}$) [9] the fraction of transmitted light versus incident light can be calculated based on the Beer–Lambert–Bouquet law as follows:

$$\log_{10}(I_0/I) = \varepsilon\, c\, l \qquad (1)$$

where, I_0 and I represent the intensity of incident and transmitted light, respectively; ε is the molar extintion coefficient; c is the DSP volume concentration and l is the path length of radiation. Using the DSP density of $\rho = 1200$ kg/m^3 [7], the calculated concentration (c) of DSP ($M_w = 284$) would be equal to 4.2 mol/L. Therefore, if $I/I_0 = 0.9$, the attenuation equals:

$$\log_{10}(0.9) = -0.046 \qquad (2)$$

and the calculated path length at the given attenuation will be equal to:

$$l = 0.046/(\varepsilon c) \sim 10\ \text{nm} \qquad (3)$$

In other words, a 10 nm thick DSP particle would be 90% transparent and would, therefore, receive nearly uniform optical illumination. Therefore, even the smallest DSP particles studied in this investigation are not optically thin, and it is unlikely that homogeneous polymerization is occurring even in the small particles produced from RESS. Rather, the demonstrated mechanical stability of the small DSP particles is most likely due to their greater ability to relieve the state of internal stress produced by the photopolymerization process.

The DSP monomer particles developed by RESS were observed to be stable for months and retained photoreactivity if stored in a dark environment at room temperature for at least one year. We also found that they can be polymerized inside a UV-transparent matrix, such as a siloxane-based polymer. These results suggest the possibility for the use of solid DSP monomer particles in coatings or in 2-D or 3-D optical data storage devices. We have also reported applications for these small monomer DSP particles in the chemical sensor field [12,22].

4. Conclusions

The production and photopolymerization of mechanically stable DSP polymer in the form of small particles was described. Small 100–300 nm DSP monomer particles were developed by rapid expansion of a supercritical chlorodifluoromethane solution. The particles obtained are free of solvent residue and, therefore, the RESS process described here can potentially eliminate the costly procedure of separating particles from a liquid solvent. The particles were found to be highly photoreactive and capable of polymerization to yield crack-free, amorphous or crystalline polymer upon UV irradiation. Experimentally it was confirmed that particle size plays a significant role in the DSP crystal fragmentation process photopolymerization rate. It was found that small DSP particles below about 0.5 μm, are mechanically stable for months and, therefore, can be polymerized either immediately after formation or at later times. The small DSP particles described in this paper can be utilized in applications such as chemical sensing, optical data storage, semiconductor devices, coatings, and sensors.

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