Polymerization of 1,4-dinitrosobenzene: Kinetics and Submicrocrystal Structure

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Abstract: In this study, the structure of the polycrystalline poly(l,4-phenyleneazine N,N-dioxide) was investigated by Scanning Electron Microscopy and related with the previously calculated molecular structure. Kinetics of polymerization of 1,4-dinitrosobenzene, prepared by both cryogenic UV photolysis and *in vacuo* deposition were measured by time-resolved FT-IR spectroscopy. Acquired data was analyzed by curve fitting with the standard Avrami-Erofeev and two-step consecutive reactions models. Activation parameters were calculated from Arrhenius and Eyring-Polanyi equations, for both models. The results obtained by using the two models, along with the goodness-of-fit parameters, were compared. It was shown that both bulk-based and reaction-based models can be used to adequately describe solid-state chemical reaction kinetics. Furthermore, a two-step consecutive reactions model is a suitable alternative to the most commonly used Avrami-Erofeev model.

Keywords: scanning electron microscopy, polymerization, kinetic models, solid state, activation parameters.

INTRODUCTION

AROMATIC C-nitroso compounds have proven to be a useful model system for the investigation of chemical reactions in the solid state.[1–3] They exist in two different forms, as nitroso compounds (monomers), and *E*- or *Z*-azodioxy compounds (dimers or polymers).[4,5] In the solid state, most aromatic C-nitroso compounds appear in the azodioxy form, but can be converted to stable or metastable monomeric forms by dissolution in organic solvents, heating, or by UV irradiation at cryogenic temperatures.[5] An important feature of the nitroso/azodioxy system is that the two forms can be easily distinguished by spectroscopic methods (UV / Vis, NMR, IR, *etc.*), which facilitates kinetic measurements.[4]

1,4-Dinitrosobenzene has been investigated because it is, next to 1,3-dinitrosobenzene, the simplest aromatic C-dinitroso compound capable of polymerization. It has been found that by deposition of 1,4-dinitrosobenzene vapor onto the surface cooled to 12 K produces a solid layer consisting only of the nitroso monomer.[6,7] Warming the sample to around 150 K causes fast polymerization. Recently, it has been found that the formation of polymers under cryogenic condition is not a simple process. The reaction on the cold surface follows the multistep mechanism. The first intermediate observed by IR spectroscopy is the *Z*-azodioxy isomer, but further warming causes the irreversible rearrangement to the *E*-isomer, and finally the formation of the stable polymer. Besides the use of cold surface deposition, 1,4-dinitrosobenzene can also be prepared photolytically. UV irradiation of the polymer encapsulated in a KBr pellet at 13 K yields monomers. However, these monomers dimerize and oligomerize exclusively to the azodioxy products with *E*-stereochemistry.

The polymerization mechanism as well as the stability of the polymer depends on the topotactic solid-state conditions.[3] It appears that monomers are more randomly distributed after cryogenic deposition, while after photolysis of the polymer the orientation of monomer molecules is more conserved, which is convenient for

repolymerization.[1,2] Also, repolymerization after photolysis depends on the regularity of the crystal structure of the starting polymer.[1] In this work, we present a morphological investigation of the polymeric material, complemented with isothermal determination of activation energies for the polymerization under cryogenic conditions.

For the analysis of isothermal polymerization, the standard Avrami-Erofeev (AE) approach is used along with the two-step consecutive reaction model (2CR). The reactions in the 2CR model can be written as:

$$R \xrightarrow{k_1} R* \xrightarrow{k_2} P \qquad (1)$$

where R, R* and P are the reactant, the activated reactant and the product, respectively. The activated reactant R* can be thought of as a transient intermediate having a property (for example, spatial arrangement) which makes the reaction facile. In phase transitions, the activated reactants can be thought of as Avrami's germ nuclei, which might or might not form into active growth nuclei.[8-10] The motivation for using 2CR is that it is a reaction-order based model, meaning that it can give additional mechanistic insights about the underlying processes, while the AE model only yields information about the overall transformation. More generally, the question is: Can reaction-order based models be used for the description of solid-state chemical reactions?

EXPERIMENTAL

Synthesis

Poly(l,4-phenyleneazine N,N-dioxide) (PNND) was prepared from cyclohexadiene-1,4-dione as previously described by Khishchenko.[11] The product was purified by vacuum sublimation, followed by condensation on a cold surface.

Microscopy

Zeiss electron microscope Gemini Supra installed at Laboratory for Microscopy and Microanalysis, University of Pretoria, RSA was used for obtaining high resolution SEM images. In Lens detector was employed at 1.7 mm. Due to very sensitive material, working voltage was set just to 600 V.

Kinetic Measurements

Samples for kinetic measurements were prepared either by photolysis of standard PNND doped KBr pellets (m(PNND) / m(KBr) ≈ 1 / 100) or by cryogenic deposition of 1,4-dinitrosobenzene vapors on a cooled KBr window. KBr pellets were secured on the cryocooler cold finger between two KBr discs and irradiated with 254 nm UV low-pressure Hg lamp (UVP R-52G). Samples were irradiated until no further changes in the IR spectra were noticeable.

Cryogenic conditions were achieved by Leybold–Heraeus ROK 10–300 cyclic helium cryostat. Isothermal kinetic measurements were performed at desired temperature after warming the samples from 13 K and holding the temperature constant. Temperature was control by Scientific Instruments model 9700 connected to a Si diode and a heater unit. Multiple measurements at different temperatures were conducted for the same sample to obtain activation parameters of repolymerization. FT-IR spectra were recorded on a PerkinElmer SpectrumTwo spectrometer, averaging 10 scans per spectrum. The background spectrum was obtained by observing ambient air. Spectra were recorded every ~ 65 s and the reactions were monitored over a 2–4 h period. Solid-state repolymerization rates were measured following the change in absorbance of the −N=O stretching at 1521 cm^{-1}, E-ONNO stretching at 1264 cm^{-1}, or Z-ONNO stretching at 1387 cm^{-1}. Baseline corrections for the spectra were performed using adaptive iteratively reweighted penalized least squares algorithm. Amount of the compound of interest was calculated according to the following equation:

$$x'_Y(t) = \frac{A_Y(t) - A_Y(t_{end})}{A_Y(t_{end}) - A_Y(t_{start})} \qquad (2)$$

where $x'_Y(t)$ is the normalized amount of compound Y present in time t, $A_Y(t_{start})$ and $A_Y(t_{end})$ are absorbances at the start and end of the measurement, respectively. Therefore, the normalized amount of the product is 0 at t_{start} and 1 at t_{end}.

Avrami-Erofeev Model

The description solid-state kinetics has proven to be a difficult problem for which a variety of solutions has been devised, with the AE model being the most prevalent.[12,13] An often used form of the AE model is:

$$x'_P(t) = x'_\infty - (x'_\infty - x'_0)\exp\left[-(kt)^m \right] \qquad (3)$$

Here, x'_∞ and x'_0 are used as fitting parameters, along with the rate constant k and the dimensionality coefficient m. This implementation of the Avrami equation often gives better variances than the standard implementation:

$$\alpha(t) = 1 - e^{-(kt)^n} \qquad (4)$$

despite having a larger number of parameters.[6] The AE model has been successfully used to describe many solid-state processes-phase transitions, nanocluster formation, crystallization and chemical reactions.[13–16]

Two-Step Consecutive Reaction Model

From [Eq. (1)], the following differential equations can be written:

$$\frac{dx'_R}{dt} = k_1 x'_R \tag{5}$$

$$\frac{dx'_{R^*}}{dt} = k_1 x'_R - k_2 x'_{R^*} \tag{6}$$

$$\frac{dx'_P}{dt} = k_2 x'_{R^*} \tag{7}$$

[Eq. (5)]–[Eq. (7)] can be analytically solved. If, x'_{R_0}, $x'_{R^*_0}$, and x'_{P_0} are the starting amounts of the reactant, activated reactant and product, the following equation can be used to calculate the amount of the product at time t:

$$x'_P(t) = x'_{R_0}\left(1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right) + x'_{R^*_0}(1 - e^{-k_2 t}) + x'_{P_0} \tag{8}$$

Calculation of Rate Constants and Activation Parameters

Data fitting was accomplished using numerical integration and nonlinear least-squares with the default simplex algorithm implemented in the Wolfram Mathematica 10.3. In the following section, we present results from the 2CR along with AE model.[17] For the AE model, four fitting parameters were used (x'_0, x'_∞, k, and m), while 2CR had five (x'_{R_0}, $x'_{R^*_0}$, x'_{P_0}, k_1 and k_2). The activation energies for both models were calculated according to the Arrhenius equation, while Gibbs energy of activation, enthalpy of activation and entropy of activation were calculated from Eyring-Polanyi equation.

RESULTS AND DISCUSSION

Morphology of the Submicrometer Particles of PNND

The freshly sublimed polymer was studied by SEM microscopy under different magnifications (Figure 2). The polymeric material has interesting morphology. By going to higher magnifications, (Figure 2A–2C) the regularity of the (poly)crystalline structure can be inferred. All of the particles are structured in layers, while some of them are also folded (Fig. 2C). The less folded crystals can be seen in figures with the largest magnification (Figure 2D–2E). In our previous paper the molecular geometries of oligomers (up to octamers) were calculated. The molecule is helical and moderately folded. From the length of the octamer, which is 5.1 ± 0.1 nm, it is possible to estimate that the number of monomeric units (1,4-dinitrosobenzene molecules) in the largest arc in Fig. 2C might be around 5×10^3. In the smallest edge of the non-folded crystal in the middle of the Fig. 2F this number might be less than 4×10^2. The observable folding which appears in larger crystalline particles is expected from the extent of molecular folding found in PNND by calculation.[6] Such a robust structure is a consequence of regular molecular arrangement and as such could be a suitable starting material for the study of the photochemical and thermochemical reaction mechanisms in the solid state.

Photodissociation and Re-dimerization

According to previous investigations, UV irradiation can be used to induce the dissociation of the azodioxy bond and formation of nitroso monomers, as evidenced by IR spectra.[6] The azodioxy bonds reform upon warming the samples. This is indicated by the decrease of the monomeric –N=O signal (1521 cm^{-1}) and the simultaneous increase of the *E*-ONNO signal (1264 cm^{-1}).
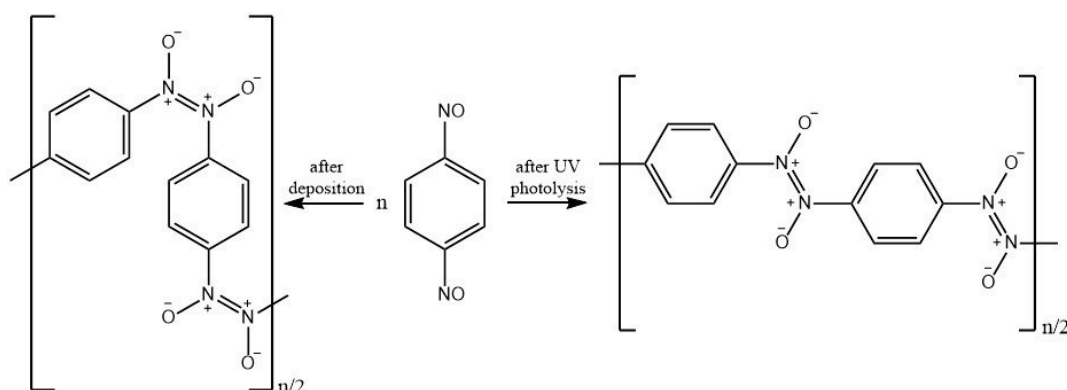
Figure 1. Schematic representation of 1,4-dinitrosobenzene polymerization after deposition onto a cold window and after cryogenic UV photolysis.
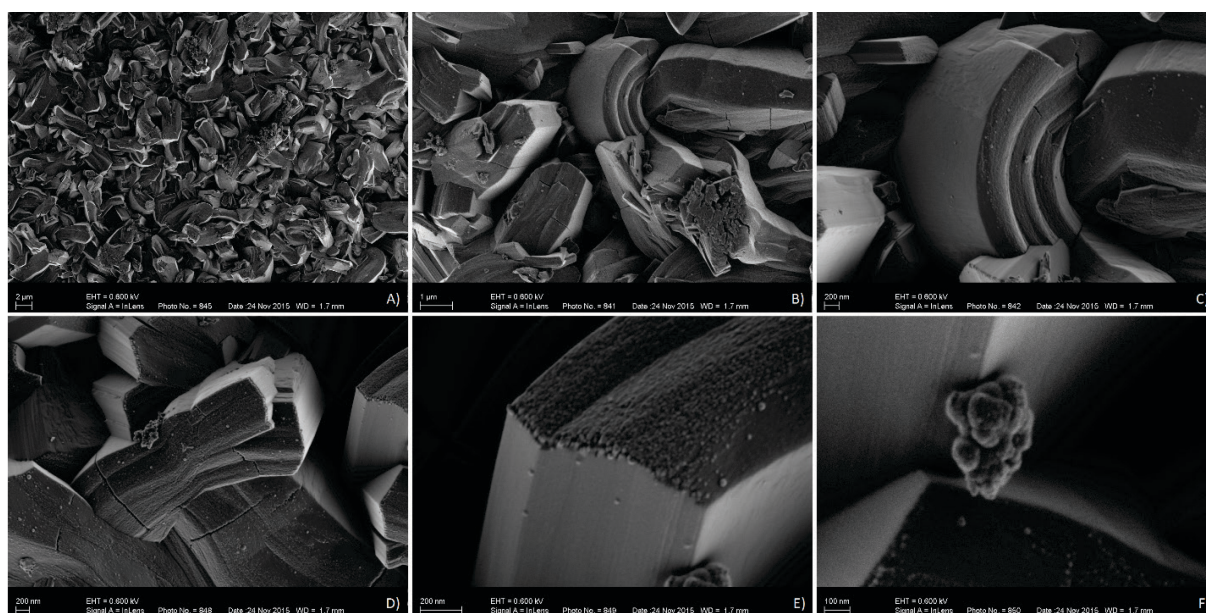
Figure 2. SEM images of the polycrystalline PNND sample at different magnifications.

The optimal temperature range for kinetic measurements of 1,4-dinitrosobenzene polymerization using IR spectroscopy is found to be between 120 and 150 K.

The repolymerization curve features a rapid growth phase, followed by significantly slower roughly linear growth, which resembles some types of aggregative processes.[13] Figure 3a shows fitted kinetic curves for 2CR (black) and AE models (orange), while residuals of the fits are shown in Figure 3b. On average, the residual sum of squares of the AE fits are 18 % larger when compared to 2CR (Table 1). As shown in Figures 3a and 3b, the difference is especially pronounced at the beginning of the curve, resulting in larger residuals for the AE model.

Table 1. Rate constants (k_2) and residual sums of squares (*RSS*) of the 2CR and AE fitted curves for experiments at different temperatures.
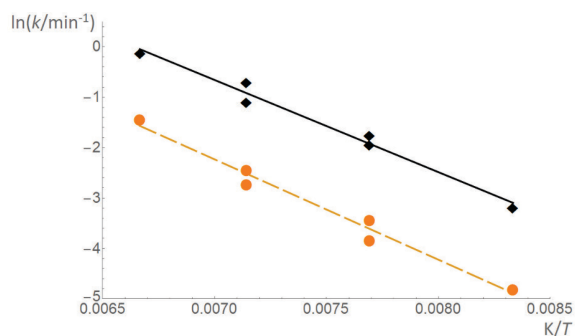
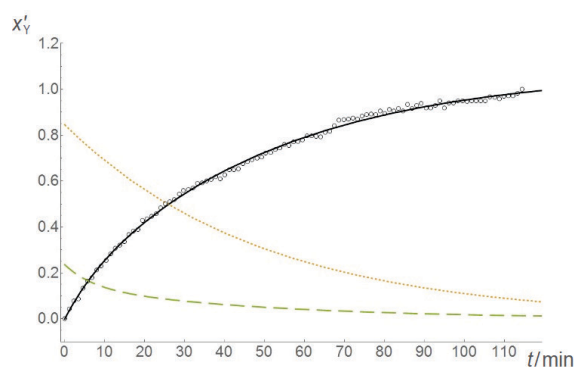| #	T / K	2CR		AE	
		$10^2\,k_2$ / min^{-1}	$10^2\,RSS$	$10^2\,k$ / min^{-1}	$10^2\,RSS$
1	120	4.09	5.33	0.815	5.52
2	130	17.3	0.229	3.21	0.237
3	130	14.4	1.35	2.15	1.44
4	140	33.3	0.174	6.49	0.263
5	140	49.1	0.488	8.92	0.770
6	150	88.2	0.628	23.6	0.736
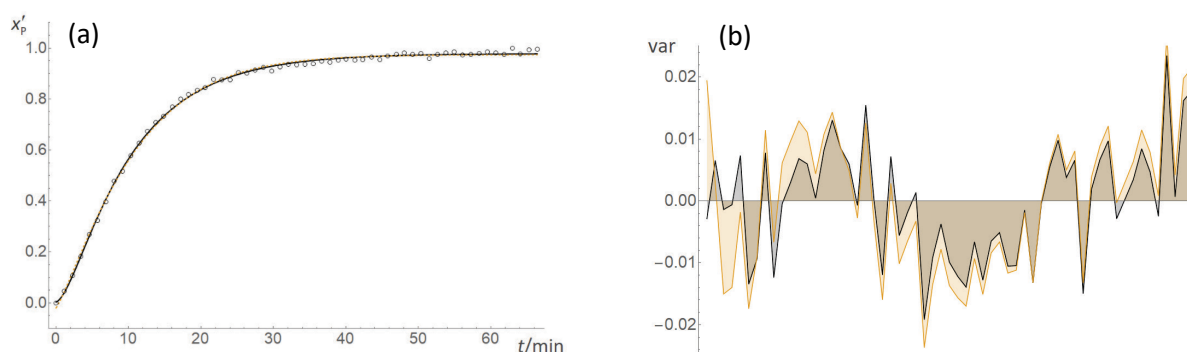
Figure 3. (a) 2CR (black) and AE (orange) fitted curves for repolymerization reaction at 140 K of the photolyzed sample; (b) 2CR (black) and AE (orange) residuals of the fitted curves for repolymerization reaction at 140 K of the photolyzed sample.

For the AE model the Arrhenius and Eyring plots are easily obtained, as there is only a single rate constant. However, in case of the 2CR model there are two rate constants, k_1 and k_2. In Figure 4, it is shown that the slope of the Arrhenius plot for the 2CR k_2 constant (black) is very similar to the one obtained for the Avrami k constant. Moreover, activation enthalpies and entropies calculated from the Eyring-Polanyi equation are independent of the used model. These results suggest that the k_2 constant of the 2CR model corresponds to the AE k constant, giving similar activation parameters, as shown in Table 2.

Important contributions of the 2CR model are the time plots of the reactant, activated reactant and product. As shown in Figure 5, some of the activated reactant is already present at the beginning of the measurement. This might be due to the imperfections in the crystal lattice of the monomer, although a possible facile interconversion between the reactant and the activated reactant cannot be ruled out. In this way, the activated reactant could be an arrangement of molecules similar to the Avrami germ nuclei.[8–10] These results, along with the Arrhenius plots, suggest that the formation of the activated reactant (by k_1) could correspond to a nucleation-type process, while the k_2 constant might characterize the chemical reaction.
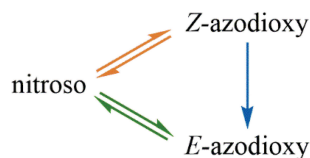
Polymerization (Dimerization) of the *in vacuo* Deposited Monomers

The IR spectra of the deposited samples, when compared to the photolyzed ones, show that different processes take place upon warming. In the deposited sample three parallel processes, displayed in Figures 6 and 7, can be noticed:
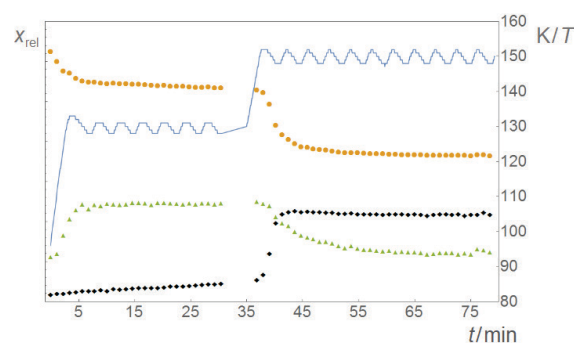
At 130 K the nitroso → *Z*-azodioxy (orange) conversion is dominant, but a relatively slow, parallel nitroso → *E*-azodioxy (green) reaction also occurs. However, by warming the sample to 150 K, a very fast, seemingly irreversible formation of the *E*-azodioxy compound takes place at the expense of the *Z*-isomer (blue). Because these three processes cannot be

Figure 4. Arrhenius plots for the 1,4-dinitrosobenzene polymerization analyzed by 2CR model (black) and AE model (orange). The 5 rate constants were obtained from a total of 422 data points.

Table 2. The calculated activation parameters for the AE and 2CR models.

	E_a / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}
AE	16.6 ± 1.3	15.5 ± 1.3	−183.0 ± 5.1
2CR (k_2)	15.2 ± 1.1	14.1 ± 1.1	−179.7 ± 9.6

Figure 6. The qualitatively observed reactions in the deposited monomers.

Figure 5. Fitted kinetic curves for reactant, R (orange), activated reactant, R* (green) and product, P (black) for the polymerization measurement at 130 K (entry 3 in Table 1) after cryogenic UV photolysis.

Figure 7. Kinetic profiles for the repolymerization reaction of the deposited sample at 130 and 150 K. Intensities of −N=O, *E*-ONNO and *Z*-ONNO stretching vibrations are shown in orange, black, and green, respectively. Temperature is indicated by the blue line.

decoupled, individual rate constants and activation parameters cannot be unambiguously determined in this temperature range.

At higher temperatures the repolymerization kinetics becomes more straightforward, following a quasi-exponential curve. Figure 8a and 8b show the kinetic curve for the repolymerization at 210 K following cryogenic deposition, analyzed by both 2CR and AE models.

The obtained k_2 and k rate constants for the repolymerization at 210 K of the deposited sample are 1.01 min^{-1} and 0.138 min^{-1}, respectively. These rate constants are, on average, 55 times lower than the ones of the photolyzed samples calculated from extrapolation to 210 K. This could indicate that the monomers in samples prepared by photolysis adopt a more favorable topochemistry for chemical reaction than the monomers obtained by deposition.

CONCLUSIONS

Time-resolved absorbances for the nitroso → azodioxy conversions of the photolyzed and deposited PNND samples were measured by IR spectroscopy. The rate
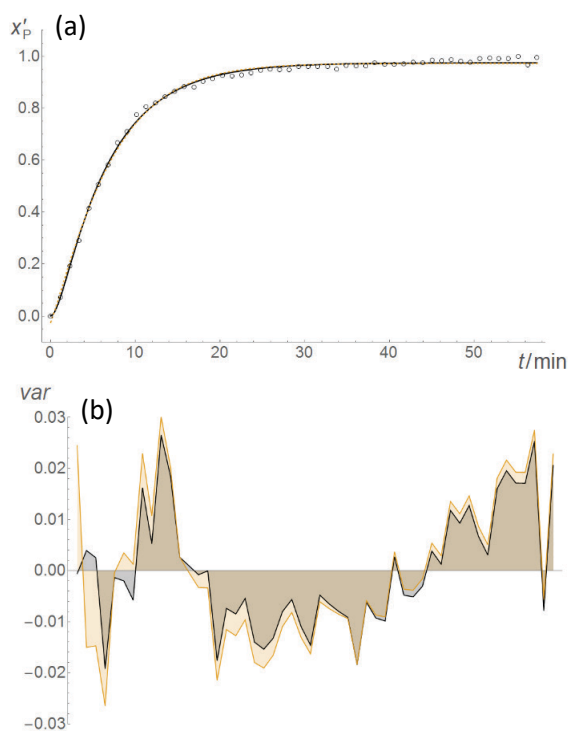
Figure 8. (a) 2CR (black) and AE (orange) fitted curves for repolymerization reaction at 210 K of the deposited sample; (b) 2CR (black) and AE (orange) residuals of the fitted curves for repolymerization reaction at 210 K of the deposited sample.

constants were obtained by curve fitting of the experimental data by both the two-step consecutive reaction (2CR) and Avrami-Erofeev (AE) models, and the corresponding activation parameters were calculated. Both obtained activation parameters were very similar, at about 15 kJ mol^{-1}, suggesting that the 2CR k_2 gives similar mechanistic information as the AE k constant. Such a low E_a value could indicate that the monomer units remain close after photolysis, which is in accord with previous findings (specifically, the N–N distances in 4-bromonitrosobenzene crystals after photolysis were found to be only 2.3 Å).[1] The overall results, both concerning fits of the individual kinetic curves and the Arrhenius plots, indicate that reaction-order based models, such as 2CR, can be used alongside the AE model to provide insights about the chemical reactions in the solid state.

The rate constants for the reaction considering the deposited samples proved troublesome to measure precisely because of the overlap of the various processes happening in the temperature range in which reaction proceeds at sufficient rate. Specifically, three coupled processes were detected: the formation of *E*- and *Z*-azodioxy compounds from monomers, and their interconversion. When compared to the extrapolated rates of the photolyzed samples, the repolymerization reactions of the deposited samples were significantly (by a factor of ≈ 50) slower.

SEM images show that PNND forms semi-regular moieties of the size of up to few mm. From comparing calculated length of polymeric chains from our previous work with the size obtained from SEM measurements, it can be concluded that PNND forms polymers of up to 5×10^3 units long.

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