

Technical Notes

Development of Combinatorial Chemistry Methods for Coatings: High-Throughput Optimization of Curing Parameters of Coatings Libraries

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An automated analytical system has been implemented for the high-throughput optimization of processing conditions such as curing parameters in fabrication of UV-cured automotive organic protective coatings. Selection of optimum process conditions of combinatorial arrays of coatings is essential to correlate the high-throughput screening and conventional processes and to achieve the desired physical properties of coatings. For monitoring of curing conditions of each coating in the array, a viscosity-sensitive fluorophore 4,4'-bis(2-benzoxazolyl)stilbene was incorporated into coating formulations. This fluorescence tagging approach permitted us to combine a gradient temperature heater and a UV curing system with the full capabilities of our high-throughput screening system, including generation of spectroscopic data and its analysis. This investigation demonstrated the possibility of rapid decoupling of temperature and radiation effects in curing of UV-curable coating formulations by using multiple coatings and process conditions at once. While the system described here was implemented for high-throughput optimization of temperature conditions of radiation curing of arrays of organic protective coatings for automotive applications, this system can be further applied for a variety of other applications where optimization of process parameters can be studied in situ or off-line using optical spectroscopic tools.

At present, combinatorial and high-throughput methods are finding applications beyond the pharmaceutical industry for discovery of materials in chemistry and materials science. These materials include catalysts, luminescent and magnetoresistive compounds, polymers, high-temperature superconductors, and many others.¹ High-throughput methods have also been employed for optimization of material compositions. Recent examples include optimization of homogeneous and heterogeneous catalysts,^{2–4} multicomponent inorganic films,⁵ and nanoscale materials.^{6, 7}

In addition to discovery and optimization of new chemical compositions, high-throughput approaches can provide important time savings in optimization of process parameters of material fabrication through parallel reactions and automation.^{8,9} However, until now, high-throughput optimization of process parameters has not been explored in much detail. The goal of this work is to develop an automated analytical system for the high-throughput optimization of processing conditions such as curing parameters in fabrication of UV-cured automotive organic protective coatings. Selection of optimum conditions for radiation curing of combinatorial arrays of coatings is essential if the process is to be correlated with the conventional curing process and the coatings are to have desired physical properties.

In the past, a variety of methods have been applied for monitoring of radiation curing of coatings. These include differential scanning calorimetry, photocalorimetry, dilatometry, microwave dielectrometry, near-IR, mid-IR, and Raman spectroscopies, fluorescence probes, laser interferometry and nephelometry, piezoelectric quartz crystal microbalances, torsional dynamic mechanical analysis, oscillating plate rheometry, and some other techniques.^{10–14} Curing parameters affecting performance of UV-

- (2) Omata, K.; Ishiguro, G.; Yamada, M. *Sekiyu Gakkaishi* **2000**, *43*, 317–319.
- (3) Zhang, Y.; Gong, X.; Zhang, H.; Larock, R. C.; Yeung, E. S. *J. Comb. Chem.* **2000**, *2*, 450–452.
- (4) Thomson, S.; Hoffmann, C.; Ruthe, S.; Schmidt, H.-W.; Schuth, F. *Appl. Catal., A* **2001**, *220*, 253–264.
- (5) Ohtomo, A.; Makino, T.; Tamura, K.; Matsumoto, Y.; Segawa, Y.; Tang, Z.; Wong, G. K. L.; Koinuma, H.; Kawasaki, M. *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, *3941*, 70–81.
- (6) Bosman, A. W.; Heumann, A.; Klaerner, G.; Benoit, D.; Frechet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2001**, *123*, 6461–6462.
- (7) Cassell, A. M.; Verma, S.; Delzeit, L.; Meyyappan, M.; Han, J. *Langmuir* **2001**, *17*, 260–264.
- (8) Newsam, J. M.; Schuth, F. *Biotechnol. Bioeng. (Comb. Chem.)* **1998/1999**, *61*, 203–216.
- (9) Rosso, V. W.; Pazdan, J. L.; Venit, J. J. *Org. Process Res. Dev.* **2001**, *5*, 294–298.
- (10) Davies, A. K. In *Radiation Curing of Polymers II*; Randell, D. R., Ed.; The Royal Society of Chemistry: Bristol, England, 1991; pp 379–399.
- (11) Rabek, J. F. In *Radiation Curing in Polymer Science and Technology. Volume I. Fundamentals and Methods*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: London, England, 1993; pp 329–452.
- (12) Krongauz, V. V.; Yohannan, R. M. *Mol. Cryst. Liq. Cryst.* **1990**, *183*, 495–503.

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(1) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2494–2532.

cured organic coatings were studied by many academic, industrial, and governmental research groups because of both fundamental and applied importance. Cure behavior was studied as a function of light intensity and wavelength, film thickness, moisture and oxygen partial pressure, and temperature.^{12–19} These studies were performed using conventional low-throughput approaches with analysis of different process conditions on a single coating at a time. Because the reaction optimization process is a trade-off between desires for best performance and least experimental investment, the increase in optimization throughput by means of parallel reactions at different process conditions and automation is highly desired.⁹

In the development of organic coatings for automotive applications using combinatorial chemistry methodology,²⁰ it is important to find the optimal temperature regime to assist in UV curing of coatings because the curing process can be accomplished under a pulsed UV source.²¹ For the high-throughput optimization of process conditions of radiation curing of arrays of organic coatings, we adapted the analytical spectroscopic tools initially developed for the accelerated determination of the most promising coating materials for their abrasion resistance.²⁰ For monitoring of curing conditions of each coating in the array, we incorporated a viscosity-sensitive fluorophore into coating formulations. Viscosity-sensitive fluorophores that change their spectral features as a function of curing condition of coatings or polymers have been used extensively in the past.^{22–25} In our hands, this fluorescence tagging approach permitted us to combine a gradient temperature heater and a UV curing system with the full capabilities of our high-throughput screening system, including generation of spectroscopic data and its analysis. This investigation demonstrated the possibility of rapid decoupling of temperature and radiation effects in curing of UV-curable coating formulations by using multiple coatings and process conditions at once.

EXPERIMENTAL SECTION

Materials. The coatings investigated were based on an acrylated aliphatic urethane oligomer (Ebecryl 8804, UCB chemicals Corp., North Augusta, SC). The fluorophore used was 4,4'-

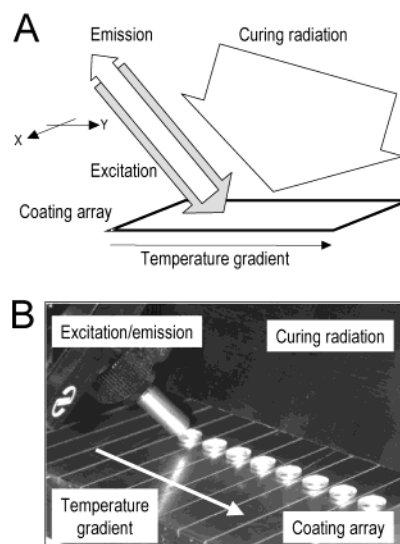


Figure 1. Measurement concept (A) and a general view (B) of a setup for the high-throughput optimization of curing conditions of arrays of UV-curable coatings.

bis(2-benzoxazolyl)stilbene (BOS; Aldrich Chemical Co., Inc., Milwaukee, WI). The fluorophore was incorporated into the uncured coating formulation by dissolving the fluorophore in chloroform and mixing this solution with a 30 wt % solution of the acrylated aliphatic urethane oligomer in methoxypropanol. About 1×10^{-5} L of the resulting solution was delivered into standard aluminum plates (~ 6 -mm diameter, 1-mm height) used for differential scanning calorimetry. The solvents were allowed to evaporate by keeping solutions at room temperature in air. The resulting coatings had a uniform thickness of $\sim 1 \times 10^{-5}$ m. The concentration of the fluorophore in the final formulation was $\sim 10^{-4}$ M.

Measurement Principle of Temperature-Dependent UV Curing. A measurement concept and a view of the setup for the high-throughput optimization of curing conditions of UV-curable coatings are presented in Figure 1. Curing radiation is applied to multiple coatings in a pulsed fashion. The tag fluorophore alters its emission property as a function of the curing condition of the coating. The condition of the coating is monitored in real time via the fluorescence signature of the tag fluorophore. Excitation of the fluorescence and collection of the emission are achieved collinearly.

High-Throughput Curing System. Multiple samples with coating formulations were arranged on a gradient heater built in-house. The curing temperatures of each sample are shown in Table 1 as measured with thermocouples positioned at appropriate locations along the heater. Curing of coating formulations was performed using a UV–visible radiation produced with a fiber-optic curing system (Novacure Spot Cure System from EFOS, Mississauga, ON, Canada). The system was equipped with a high-pressure 100-W Hg vapor short arc lamp. The light from the source was coupled into an extended spectral range liquid-core optical waveguide (8-mm diameter, 1-m length, made by EFOS) and a 10-cm-long fiber-optic line spreader (EFOS) that converted the round light beam propagating in the waveguide into a 10-cm-long and 2-mm-wide light line. Curing was accomplished in air by a periodic exposure of the coatings to the UV–visible radiation

- (13) Lange, J.; Davison, J. W.; Hult, A. *Polym. Mater. Sci. Eng.* **1997**, 76, 542–543.
- (14) Lovell, L. G.; Lu, H.; Elliott, J. E.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.* **2001**, 17, 504–511.
- (15) Beech, J. C.; Turner, C. H. C. *J. Chem. Technol. Biotechnol., Chem. Technol.* **1983**, 33A, 63–69.
- (16) Krongauz, V. V.; Schmelzer, E. R.; Yohannan, R. M. *Polymer* **1991**, 32, 1654–1662.
- (17) Tilley, M. G.; Trapp, M.; Webb, K. In *RadTech '92 North Am. UV/EB Conf. Expo., Conf. Proc.*; RadTech Int. North Am.: Northbrook, IL, 1992; Vol. 1, pp 48–56.
- (18) Kan, L.; Kao, K. C. *J. Chem. Phys.* **1993**, 98, 3445–3451.
- (19) Yoshizawa, J.; Naito, Y.; Takase, H.; Komiya, Z.; Ukachi, T. *Proc. Int. Wire Cable Symp.* **1999**, 48, 680–686.
- (20) Potyrailo, R. A.; Chisholm, B. J.; Olson, D. R.; Brennan, M. J.; Molaison, C. A. *Anal. Chem.* **2002**, 74, 5105–5111.
- (21) Saunders, D. L.; Akhave, J. R.; Potyrailo, R. A.; Olson, D. R.; Flanagan, W. P. An improved combinatorial testing method and apparatus for coat material formulations and methods. World Patent Application WO0132320, 2001.
- (22) Loutfy, R. O. *Macromolecules* **1981**, 14, 270–275.
- (23) Loutfy, R. O. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, 20, 825–835.
- (24) Vatanparast, R.; Li, S.; Hakala, K.; Lemmetyinen, H. *Macromolecules* **2000**, 33, 438–443.
- (25) Hakala, K.; Vatanparast, R.; Li, S.; Peinado, C.; Bosch, P.; Catalina, F.; Lemmetyinen, H. *Macromolecules* **2000**, 33, 5954–5959.

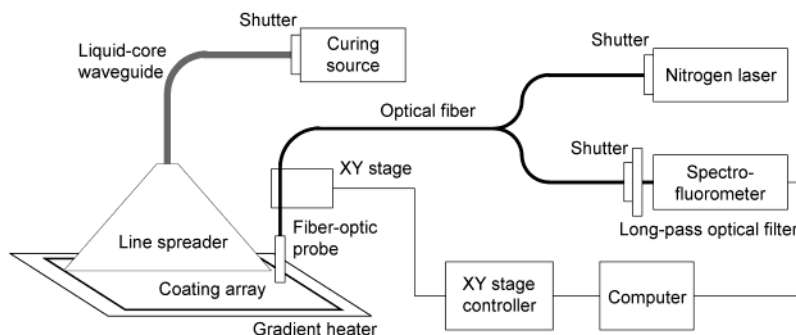


Figure 2. Schematic of the experimental setup for the high-throughput curing of coatings arrays and fluorescence analysis of the temperature dependence of cure rate for UV-curable coatings.

Table 1. Curing Temperatures of Each Sample

sample position	curing temp, °C
1	26
2	42
3	56
4	70
5	85
6	100
7	115

for 60 s every 200 s. The illumination was performed by positioning the fiber-optic line spreader at a $\sim 45^\circ$ angle to the coating surface at a distance of ~ 5 mm.

High-Throughput Analysis Setup. An experimental setup for curing and automated monitoring of curing of arrays of coatings is shown in Figure 2. Fluorescence measurements of curing of the array of coatings were performed using a nitrogen laser, a portable spectrofluorometer, and a translation stage. The laser (emission wavelength, 337.1 nm, Photon Technology International, London, ON, Canada) was operated with a 20-Hz repetition rate with a maximum average power of ~ 50 mW, maximum energy per pulse of ~ 2.8 mJ, and pulse width of ~ 800 ps. The spectrofluorometer (Ocean Optics, Inc., Dunedin, FL, model ST2000) was equipped with a $200\text{-}\mu\text{m}$ slit, 600 grooves/mm grating blazed at 400 nm and covering the spectral range from 250 to 800 nm with efficiency greater than 30%, and a linear CCD array detector. Light from the laser was focused into one of the arms of a "six-around-one" bifurcated fiber-optic reflection probe (Ocean Optics, Inc., model R400-7-UV/VIS). Emission light from the sample was collected when the common end of the fiber-optic probe was positioned near the sample at a 45° angle to the normal to the surface. The second arm of the probe was coupled to the spectrometer. Excitation light was blocked from entering the spectrometer with a long-pass optical filter. The common end of the fiber optic probe was arranged on an X–Y translation stage (Parker Hannifin Corp., Irwin, PA). The data acquisition and an automatic control of the X–Y translation stage were achieved with a computer using a program written in LabVIEW (National Instruments, Austin, TX). The program provided an adequate control of the data acquisition parameters and real-time communication with the translation stage. Four replicate measurements of fluorescence spectra were performed between pulses of curing radiation. Processing of collected spectra was performed

using KaleidaGraph (Synergy Software, Reading, PA) and Matlab (The Mathworks Inc., Natick, MA). For the evaluation of curing conditions, an intensity ratio at two wavelengths of the fluorescence emission spectra (432 and 488 nm) of the fluorophore was calculated as I_{488}/I_{432} ratio after a baseline subtraction.

RESULTS AND DISCUSSION

Spectral Characteristics Of BOS Fluorophore at Different

Temperatures. A large variety of organic fluorescent dyes have been applied for monitoring of the curing process and temperature in the past.^{22–28} From thermodynamic considerations, these dyes exhibit a temperature dependence of fluorescence quantum yield. Therefore, determination of curing effects at different temperatures could be problematic with these dyes if the temperature variation induces additional modulation of emission parameters and if a high temperature destroys a selected dye. The fluorophore selected for this work was previously used for characterization of polymers during processing and has demonstrated a temperature stability up to 300°C .²⁹ In this study, the maximum curing temperature was 115°C because of the need of preserving a polymer substrate in real applications.²⁰ Another potential problem of applications of fluorescent tags for monitoring of UV curing is photobleaching. However, the BOS fluorophore is known for its good photostability.³⁰ In addition, fluorescence ratiometric measurements implemented in this study compensate for photobleaching effects.³¹

Fluorescence spectra of the BOS fluorophore in the uncured array of coatings at different temperatures are presented in Figure 3A. These spectra demonstrate that quantum yield of fluorescence of this fluorophore is affected by temperature in the range of interest from room temperature to 115°C . However, we have found that the ratio of the emission bands of the fluorophore at 488 and 432 nm remains almost constant over the studied temperature range in uncured coating formulations. The Arrhenius plot shown in Figure 3B demonstrates that the fluorescence intensity ratio I_{488}/I_{432} has only a negligible temperature depen-

(26) Fister, J. C., III; Rank, D.; Harris, J. M. *Anal. Chem.* **1995**, *67*, 4269–4275.

(27) Figueroa, I. D.; Baraka, M. E.; Quiñones, E.; Rosario, O.; Deumíe, M. *Anal. Chem.* **1998**, *70*, 3974–3977.

(28) Ross, D.; Gaitan, M.; Locascio, L. E. *Anal. Chem.* **2001**, *73*, 4117–4123.

(29) Bur, A. J.; Roth, S. C.; Thomas, C. L. *Rev. Sci. Instrum.* **2000**, *71*, 1516–1523.

(30) Nobbs, J. H.; Bower, D. I.; Ward, I. M.; Patterson, D. *Polymer* **1974**, *15*, 287–300.

(31) Potyrailo, R. A.; Conrad, R. C.; Ellington, A. D.; Hieftje, G. M. *Anal. Chem.* **1998**, *70*, 3419–3425.

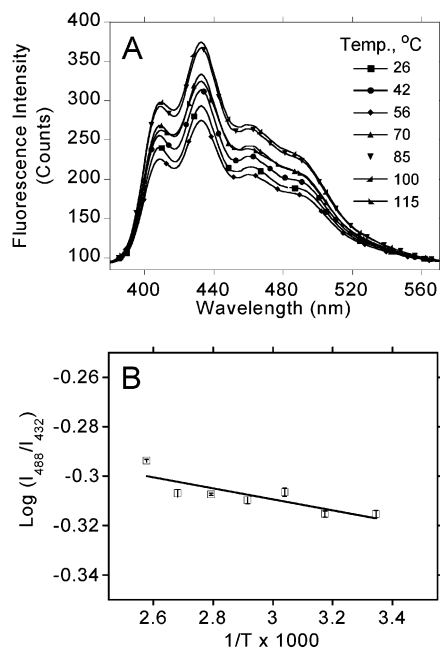


Figure 3. Temperature dependence of fluorescence of BOS fluorophore tag at temperatures ranging from 26 to 115 °C: (A) uncorrected fluorescence spectra; (B) Arrhenius plot of fluorescence intensity ratio I_{488}/I_{432} . Each data point in (B) is the mean of four replicate measurements; error bars are one standard deviation.

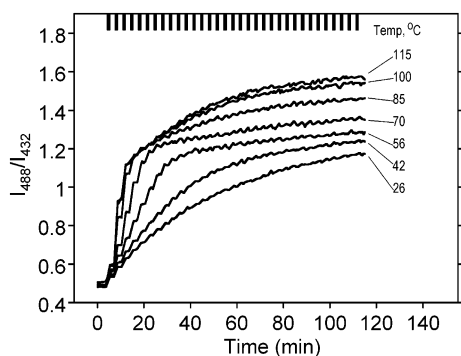


Figure 4. Temporal evolution of the fluorescence intensity ratio (I_{488}/I_{432}) of BOS fluorophore in the curing process of the array of coatings at different temperatures ranging from 26 to 115 °C. The vertical lines represent periodic 60-s-long exposures of the array of coatings to UV-visible curing radiation.

dence over the temperature range from 26 to 115 °C. This finding permits a straightforward determination of curing conditions at different temperatures using this tag fluorophore.

Temperature-Modulated Curing Kinetics. Temporal evolution of the fluorescence intensity ratio I_{488}/I_{432} of BOS fluorophore in the curing process of the array of coatings at different temperatures ranging from 26 to 115 °C is presented in Figure 4. The vertical lines represent periodic 60-s long exposures of the array of coatings to UV-visible curing radiation. The increase of the ratio of fluorescence intensities at 488 and 432 nm, I_{488}/I_{432} , indicates the curing of the studied array of coatings. This figure illustrates several important findings. First, the curing rate of the coating formulations has strong temperature dependence. Second, at the advanced phase of the curing experiment, the formulations had different degrees of cure proportional to the temperature. Third, an additional curing mechanism is present at curing

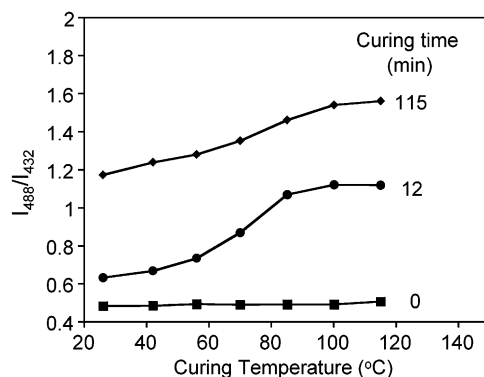


Figure 5. Fluorescence intensity ratio (I_{488}/I_{432}) of BOS fluorophore in the curing process of the array of coatings as a function of coating temperature before curing, during the initial phase of curing (12 min), and advanced phase of curing (115 min).

temperatures above 70 °C. This additional curing mechanism is evident by the change in the slope of the curing kinetics curve.

Fluorescence intensity ratio I_{488}/I_{432} of the BOS fluorophore in the curing process of the array of coatings as a function of coating temperature before curing, during the initial phase of curing (12 min), and advanced phase of curing (115 min) is depicted in Figure 5. This figure illustrates that, before curing with the UV-visible radiation, the coatings at different temperatures have the same initial conditions. Upon curing, the relative curing rate for different temperatures is preserved throughout all curing phases. An optimal temperature range for the radiation curing was found to be 90–100 °C. This is the minimal temperature at which the maximum of curing can be performed and above which a further temperature increase does not significantly increase the cured condition. Determination of this smallest curing temperature is important from the throughput and production standpoint in order to increase the throughput in screening of different coating formulations and to minimize the energy requirements needed for adequate curing of coatings.

Evaluation of Spontaneous Curing in the Dark. Examination of the initial region of the temporal evolution of the fluorescence intensity ratio I_{488}/I_{432} of the BOS fluorophore in the curing process of the array of coatings at different temperatures was performed to study the temperature-induced curing effect in the absence of curing radiation. Results of this analysis are shown in Figure 6. Three horizontal bars represent exposures of coatings to UV-visible curing radiation. This figure illustrates that temperature alone does not contribute to curing of coatings. This is evidenced from the zero slope of the curing process before the first UV-visible pulse is applied and during the measurements of fluorescence between the curing pulses. A similar approach can also be useful for the high-throughput analysis of “dark reactions” to evaluate any possible benefits of postbaking in radiation-cured coating formulations. Detailed analysis of these effects is within the scope of a separate report.

Measurement Throughput of the Developed System. Single-channel analytical systems (also known as scanning systems) have been used extensively for high-throughput screening of arrays of materials.¹ These systems are applicable for postre-

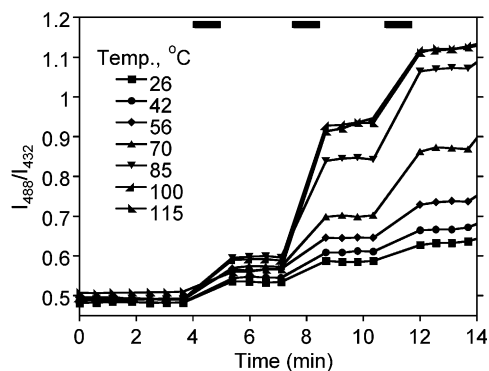


Figure 6. Initial region of the temporal evolution of the fluorescence intensity ratio (I_{488}/I_{432}) of BOS fluorophore in the curing process of the array of coatings at different temperatures ranging from 26 to 115 °C. Three horizontal bars represent 60-s-long exposures to UV–visinle curing radiation.

action measurements^{32–34} and for real-time reaction monitoring.^{35,36} In the latter case, fast chemical reactions can be conducted sequentially and monitored one reaction at a time.³⁵ Alternatively, relatively slow chemical reactions can be conducted in parallel and monitored with a fast-scanning system.³⁶

For an efficient real-time monitoring of parallel chemical reactions with a scanning system, it is critical that the time required for scanning the materials array would be much less than the time constants of the monitored reactions. In our developed system, the measurement time for each coating was only several seconds while the temperature-dependent kinetics of curing was much slower, ranging from 10 to 70 min (50% signal change). The fast scanning speed of the spectroscopic probe provided the capability of monitoring 96 regions of a standard 8×12 microtiter

array format in 2–5 min depending on the integration time selected for the adequate signal-to-noise ratio.

CONCLUSIONS

The combinatorial and high-throughput experimentation infrastructure developed for screening of new coating materials has been implemented for the high-throughput optimization of process parameters. The developed high-throughput process optimization method provided means for rapid determination of optimal curing temperature for UV curing of coating arrays. An understanding of the relationship between level of radiation cure and needed temperature under pulsed UV curing conditions is important for the implementation of in situ curing into the combinatorial factory since UV dose and temperature could be independently applied.²¹ The determination of curing conditions of coatings has been evaluated as a possible means (i) to discriminate between thermal- and UV-induced contributions to curing and (ii) to determine the point of an adequate cure.

While the analytical system developed here was implemented for high-throughput optimization of temperature conditions of radiation curing of arrays of organic protective coatings for automotive applications, this system can be further applied for a variety of other applications where optimization of process parameters can be studied in situ or off-line using optical spectroscopic tools. The number of process parameters for optimization can be easily increased to include other parameters of interest. Also, more complicated optimization procedures can be employed to correlate the process parameters with the end-use performance.²⁰

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- (32) Wang, J.; Yoo, Y.; Gao, C.; Takeuchi, I.; Sun, X.; Chang, H.; Xiang, X.-D.; Schultz, P. G. *Science* **1998**, *279*, 1712–1714.
- (33) Szurdoki, F.; Ren, D.; Walt, D. R. *Anal. Chem.* **2000**, *72*, 5250–5257.
- (34) Schiedel, M.-S.; Briehn, C. A.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4677–4680.
- (35) Cong, P.; Doolen, R. D.; Fan, Q.; Giaquinta, D. M.; Guan, S.; McFarland, E. W.; Poojary, D. M.; Self, K. W.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 484–488.
- (36) Copeland, G. T.; Miller, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 4306–4307.