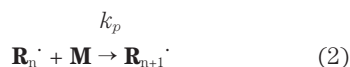# Post-Polymerization

By Igor V. Khudyakov, Ph.D., D.Sc.

UV-curing technology is often selected because of the high-speed nature of the process. Although curing is initiated by UV irradiation, polymerization continues in the dark following irradiation. For the purpose of this paper, chemistry that occurs after irradiation is defined as post-polymerization.

The kinetics of free-radical UV curing of vinyl monomers in solution is well-known. The cessation of irradiation of the photoinitiator (PI) in the presence of a monomer (**M**) quickly leads to termination of polymerization due to lack of new radicals from the PI.[1] Reactive macro-radicals, which exist in the solution at the moment irradiation is stopped, undergo primarily bimolecular termination:

$$\mathbf{R}_n{}^\cdot + \mathbf{R}_m{}^\cdot \xrightarrow{k_t} \text{macromolecule} \quad (1)$$

While "dying," macro-radicals react with the monomer:

$$\mathbf{R}_n{}^\cdot + \mathbf{M} \xrightarrow{k_p} \mathbf{R}_{n+1}{}^\cdot \quad (2)$$

Reaction 2 which produces the desired polymer occurs without irradiation and this "dark reaction" is part of the post-polymerization process. It is a common assumption that there is no difference in reactivity of $\mathbf{R}_n{}^\cdot$ at large **n,** and that reaction 2 does not affect the inevitable decay in reaction 1 of $\mathbf{R}_n{}^\cdot$. Rate constants k_p and k_t are constants of rate propagation and termination, respectively.[2] Several research groups have studied dark-polymerization reaction kinetics and properties of photopolymer systems, and introduction may be found in references 3 and 4.

Formal kinetics leads to the following simple equation for post-polymerization:

$$[\mathbf{M}]_t = \frac{[\mathbf{M}]_o}{(1 + k_t[\mathbf{R}_n{}^\cdot]_o t)^{k_t/k_p}} \quad (3)$$

Here a subscript "o" stands for the initial moment when post-polymerization is initiated. $[\mathbf{R}_n{}^\cdot]_o$ is the initial concentration of macro-radicals at the moment when irradiation is terminated. For vinyl monomers in solution $k_t/k_p \gg 1$, and post-polymerization leads to a negligible additional consumption of **M** (formation of polymer). The rate constants k_p and k_t (each has dimension of $M^{-1} \cdot s^{-1}$) characterizes the free-radical polymerization chain reaction in solution. The rate constant of an elementary bimolecular reaction in a diluted solution does not depend upon time or concentration of reagents but depends only upon temperature and pressure. This applies in particular to k_p and k_t in chain chlorination reactions and thermo- or photoinitiated oxidation of hydrocarbons by molecular oxygen.

This analysis provides a good approximation for polymerization of diluted solutions of vinyl monomers **M** in inert solvents as long as the concentration of monomer [**M**] is not higher than few mol/L.

Former kinetic does not apply for the polymerization of neat vinyl monomers. An example is the polymerization of methyl methacrylate (**MMA**), at conversions $\xi > 5\text{-}10\%$. It becomes even more unacceptable for polymerization of polyfunctional monomers—such as 1,6-hexanediol

FIGURE 1

RT-IR device

A fiber optic source is used to provide continuous or pulsed irradiation of a sample on a diamond crystal of IR spectrometer (attenuated total reflection sampling technique).

that change the effective chemical activity of the reactive species. These factors significantly impacting kinetics in the solid state may be applied to analysis of polymerization kinetics at high conversion.[5]

Experimental Techniques for Measurement of Kinetics of Post-Polymerization and Polymerization

There are a number of experimental techniques to measure the kinetics of the curing of coatings. One useful method involves measuring the disappearance of vinyl; in particular, that of the (meth)acrylate group, with real-time IR (RT-IR) spectroscopy. Figure 1 shows a typical RT-IR system. RT-IR allows measurement of the concentration (by absorption of the characteristic IR band) of acrylate with time to yield a kinetic curve.

Another method to follow the kinetics is to measure the heat evolved in the UV-curing process. Acrylates can be compared to a fuel which burns and produces heat. Polymerization of acrylates leads to a release of heat, namely ca. 80 kJ/mol (per mole of polymerized acrylate) at room

diacrylate (**HDDA**) which is widely used in the coating industry. In this case, it is believed that micro-gelation occurs after as little as 5-10% conversion of the acrylate monomer. At conversions of ~10% or more, the media is not a homogeneous solvent. The reactivity of $\mathbf{R}_n\cdot$ becomes quite different as the chain reaction is propagated. The typical UV curing of coatings is a dramatic transformation of a viscous liquid into hard or elastic film occurring in seconds and accompanied by contraction of a sample. Simple chemical kinetics and a notion of a *rate constant* for such systems are not applicable.[5,6] This fact does not prevent other analyses of the kinetics of the UV-curing process.[5,7] An accurate kinetic model is desirable for predicting performance of UV-curing systems. The model is most useful if it can be applied to a wide range of coating systems that may be used.

There are a number of successful kinetics models of bulk polymerization of monofunctional vinyl monomers. These models are mainly based on

the dependence of diffusivity and/or reactivity at a high conversion on the free volume of a system. It is known that the kinetics of reactions in a solid state are much different than kinetics in the liquid state due to differences in diffusivity of radical sites and unreacted monomer, and other factors
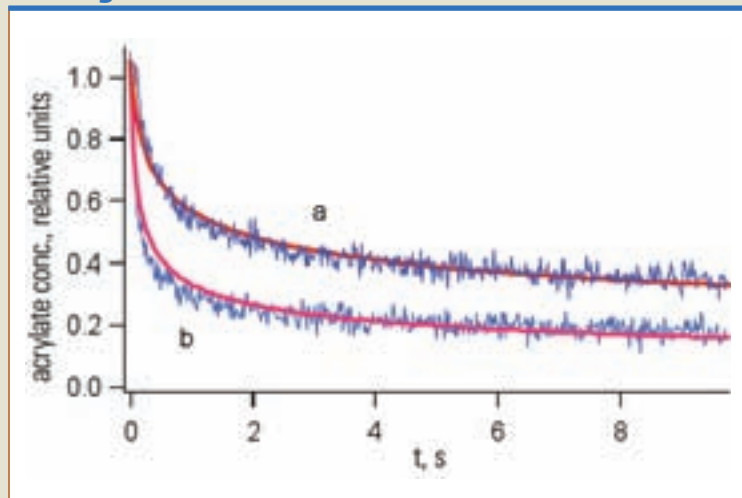
FIGURE 2

Photo-DSC device

Lamp and power source are on the left. Sample and reference pans are irradiated simultaneously through quartz windows on the sample compartment at the top of the DSC unit.

FIGURE 3

RT-IR showing post-polymerization of commercial coating with two irradiations terminated at t=0

Multiple publications present a large number of kinetic curves of cure obtained by these methods. These observations are done for a specific formulation under specific experimental conditions. The cures may be used to develop complex kinetic models; however, it is impossible to deconstruct experimental kinetic data to elementary rate constants by analyzing experimental kinetic curves of the solventless compositions.

Post-polymerization in Viscous Acrylates

Earlier, we mentioned the insignificant role of post-polymerization of vinyl monomers in solution. The situation is quite different in the UV curing of neat coatings. Termination of irradiation does not result in a quick cessation of polymerization. Reaction 1 occurs relatively slowly in a viscous media with a formed or forming polymer network. In a number of cases, especially in rigid polymer films with a high T_g, macro-radicals ($\mathbf{R_n}^{\cdot}$) can be

temperature. The equipment used to measure the heat evolved is a photo differential scanning calorimeter (Photo-DSC). A typical Photo-DSC device is shown in Figure 2. Measurement of the evolution of heat versus time under irradiation of acrylates allows for the capture of a kinetic curve. This provides an indirect measurement of kinetics of polymerization. The conversion of a coating being cured can be estimated by Photo-DSC. An example is a specimen containing 0.2 mole of acrylate observed to release 6.0 kJ of heat under UV cure. If all of the acrylate polymerizes ($\xi = 1.0$), one expects to get $0.2 \cdot 80 = 16$ kJ of heat. Thus, the conversion is approximately $\xi = 6/16 = 0.38$ or 38%.[8]

Many authors consider the maximum value of a Photo-DSC exotherm as the maximum cure rate. By comparing the rates of cure of different formulations under the same conditions (light source, temperature, etc.), one can compare the maximum cure rate of each formulation.

Another device known as a cure monitor uses the emission spectrum of a probe compound that is added at low levels to the coating. The probe is sensitive to changes in the properties of media upon cure. Measurement of the probe emission as a function of time produces a characteristic kinetic profile.

FIGURE 4

RT-IR measurements of kinetics of post-polymerization of a tetrafunctional monomer

Pulses of UV irradiation of various durations are shown

Samples were run at room temperature in air. Solid curves are fit using equation 3.
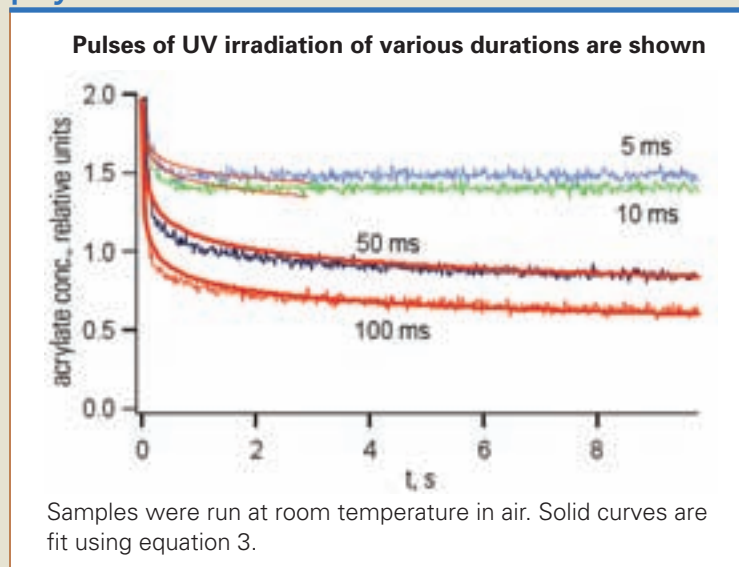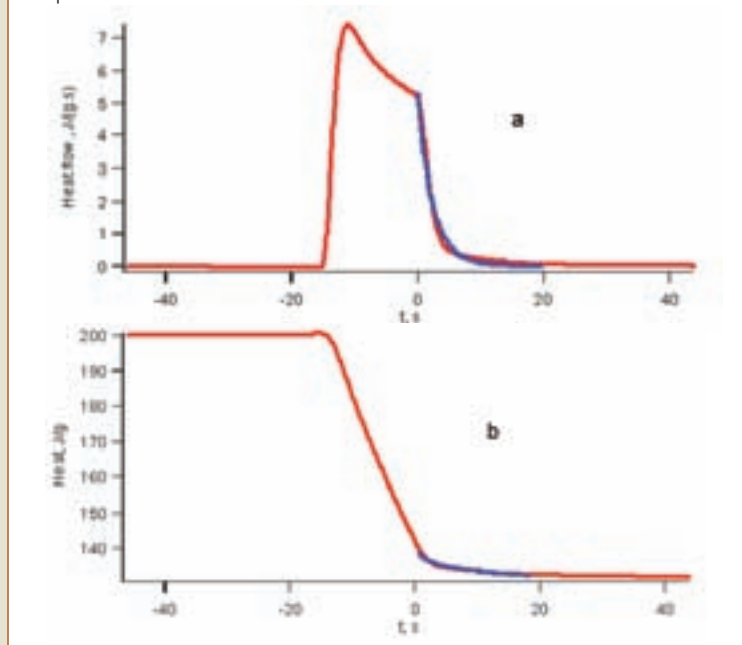
FIGURE 5

PhotoDSC traces from the UV curing of industrial coating

5a shows heat flow versus time during UV cure of a commercial coating while 5b shows the total integrated heat evolved versus time. Blue curves on Figures 5a and 5b show a curve fit using equation 3.

experimentally detected by electron spin resonance for days or even months after the completion of UV exposure. During their slow decay in coatings, $\mathbf{R}_n{}^{\cdot}$ can participate in significant post-polymerization (2) essentially increasing the degree of cure.

Figure 3 shows post-polymerization using RT-IR measurements. In this case, two different air-saturated commercial acrylate-based coatings were irradiated for a short time at room temperature. Here and in Figures 4 and 5 irradiation was terminated at the moment indicated as t=0. One can see additional conversion (50-80%) of acrylates in the dark continuing for about 10 seconds following irradiation.

The red curves in Figure 3 are a model of post-polymerization based on equation 3a where a and b are fitting parameters:

$$[\mathbf{M}]_t = \frac{[\mathbf{M}]_o}{(1 + a \cdot t)^b}; \qquad (3a)$$

The fit of the cure does not imply the validity of equation 3. It is one of many possible equations which would satisfactorily describe experimental kinetics. Usually two exponents describe almost any smooth curve with a moderate signal to noise ratio.[8]

Figure 4 shows the post-polymerization of a tetrafunctional monomer (ethoxylated **PET4A**, Sartomer SR494) containing PI. Pulses of UV irradiation of various durations were used. The results show that the longer the irradiation time, the higher the conversion ξ of the monomer. It also shows that post-polymerization becomes more pronounced with

longer exposure times which are likely the result of the formation of a more viscous media.

Similar data showing an important contribution of post-polymerization were obtained by PhotoDSC (Figure 5). Heat continues to evolve for the coating following cessation of UV exposure at t=0.

Practical Applications

The significant role of post-polymerization in the cure of coatings was shown. It is important to consider these effects in commercial coating processes. An example involves the high-speed coating of a fiber. The goal may be to run the process as fast as possible in order to increase productivity. Irradiation with one lamp system is not enough for high production speeds (fiber draw speed) in order to get a desired cure. Two lamp systems are used. There are two options—position lamps very close to each other (Figure 6a) or at a certain distance (Figure 6b).

We expect more efficient cure in case "b" because the coating undergoes two post-polymerizations steps, whereas in case "a" one post-polymerization occurs. This concept was tested and confirmed in the curing of a coating on optical fiber. Increased distance between processors resulted in a higher (ξ).[9]

Another important effect related to post-polymerization is the mechanical properties of the cured coatings. This includes tensile properties (elongation, tensile strength and modulus), as well as hardness (Durometer), abrasion resistance (scratch, mar) and toughness. These properties can change after the coating is cured. Changes in mechanical properties can be caused by two different phenomena. First, as discussed earlier, post-polymerization can occur leading to further increases in

FIGURE 6

Possible arrangement of two lamp systems for fiber curing

a) close to each other; b) at a certain distance from each other. Horizontal arrow demonstrates a direction of fiber movement.
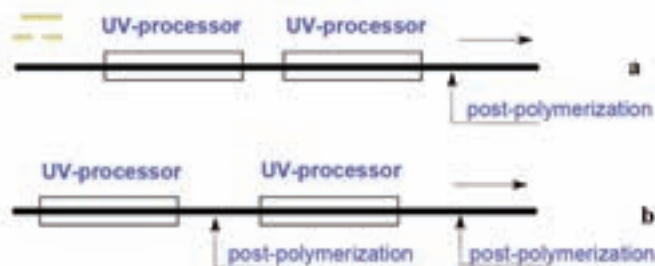
conversion. Second, a polymer matrix is expected to adopt a configuration with a minimum of free energy ($\Delta G°$). This process is relatively slow compared to post-polymerization. In most cases, *chemical reactions* occur faster than mechanical relaxation and other effects which could be called *physical processes*.[10] This suggests that mechanical properties should be measured some time after cure (for example, a minimum of 24 hours after cure). This effect was verified by testing two different cured coatings. Coating **A** formed a "hard" film upon cure, whereas coating **B** formed a "soft" film upon curing. Table 1 shows mechanical properties of these coatings measured at different times after cure.

Conclusions

Post-polymerization plays an important role in the UV curing of acrylate-based coatings—often leading to a significant additional conversion of reactive groups. It is difficult to provide a simple kinetic model of these effects; however, they can be clearly observed in multiple real-time kinetic measurement systems. Another factor influencing the mechanical properties is the relaxation of the polymer matrix that occurs after exposure and continues after post-polymerization. As a result of these post irradiation effects, more consistent results will be obtained by characterizing the materials sometime after the initial curing. Sources listed in reference 11

are recommended for those readers who are interested in more detailed and rigorous studies of post-polymerization and physical processes accompanying photopolymerization of coatings. ▶

References

1. We use here a common term accepted in the industry *UV-cure*. A better term is *photopolymerization*. Visible light and even in some special cases IR light can initiate photopolymerization.

2. Reactions 1,2 do not exhaust all reactions with participation of $\mathbf{R}_n\cdot$ even in relatively simple cases of polymerization of vinyl monomers in solution. Macroradicals participate in chain transfer to solvent, reaction with dioxygen or with traces of O_2, undergo intramolecular cyclization, react with a radical of PI, etc. In most cases, such processes are considered as side reactions.

3. Fouassier, J.P. *Photoinitiation, Photopolymerization, Photocuring: Fundamentals and Applications*, Hanser, Munich, 1995.

4. Glöckner, P. et al. *Radiation Curing. Coatings and Printing Inks,* Vincentz, Hannover, 2008.

5. Khudyakov; I. V., Purvis M.B., Turro, N. J. 2003, In *Photoinitiated Polymerization*; Belfield, K.D.; Crivello, J.K., Eds; ACS Symposium Series 847; American Chemical Society, Washington, DC, p. 113; Caspar, J.V.; Khudyakov, I.V.; Turro, N.J.; Weed G.C. Macromol. 1995, 28, 636.

6. There are European and some other research groups that carefully study polymerization of vinyl monomers such as MMA and other methacrylates, acrylonitrile, styrene, alkyl acrylates, N-vinyl formamide. Surprisingly, reliable rate constants for

TABLE 1

Mechanical properties of coatings A and B measured at different times after cure

Coating	T_g, (deg C)	Elongation to break, 1 h (%)	Modulus, 1 h (MPa)	Elongation to break, 1 day (%)	Modulus, 1 day (MPa)	Elongation to break, 3 days (%)	Modulus, 3 days (MPa)	Elongation to break 7 days (%)	Modulus, 7 days (MPa)
A	40	56	76	52	79	49	80	44	81
B	-38	350	0.8	323	1.0	312	1.3	307	1.4

T_g was measured one week after cure of coatings and is ± 2 °C.

polymerization of common monomers have become available only in the last 25 years due to development of pulse-laser polymerization techniques, cf. e.g.: Junkers, T. et. al., *Polym. Chem.* 2010, 1, 438; Willemse, R.X.E.; van Herk A.M. *Macromol. Chem. Phys.* 2010, 211, 539; Stach, M. et . al., *ibid.* p. 580; Stiegmann, R. et. al., *ibid.* p.546; Taylor, D.R., *ibid.,* p. 563. The cited publications avoid the term *rate constant* but use the term propagation and termination *rate coefficient.* k_t is often presented as $<k_t>$, which is a chain average coefficient. It is not clear how to use this wealth of information in the kinetics of UV cure of coatings.

7. Khudyakov, I.V.; Purvis, M.B.; Overton, B. J. 2002, In *Proceedings of RadTech,* Indianapolis, IN, p. 269.

8. Khudyakov, I.V.; Legg, J.C.; Purvis, M.B.; Overton, B.J. *Ind. Eng. Chem. Res.* 1999, 38, 3353.

9. The validity of such a recommendation should be verified in each case. In particular, the coating may cool down during an increased time between irradiations and that can lead to a lower ξ for certain coatings.

10. Kloosterboer, J. G. et al. *Polym. Commun.* 1984, 25, 322; Kloostoboer, J. G. *Adv. Polym. Sci.* 1987, 84, 132.

11. Dušek, K. *Polymer Gels and Networks*, 1996, 4, 383; Bressers, H.; Kloostoboer, J.G. *Polym. Bull.* 1980, 2, 201; Kloostoboer, J. G.; Bressers H. *Polym. Bull.* 1980, 2, 205; Kloostoboer, J. G.; Lijten, G.; Greidanus, F. *Polymer Comm.* 1980, 27, 268; Dušek, K., Galina, H.; Mikes, J. *Polym. Bull.* 1980, 3, 19; Boots, H.; Pandey, R.J. *Polym. Bull.* 1984, 11, 415; Boots, H.; Kloostoboer, J. G. Van dei Hei, G. R.; Pandey. R. *Brit. Polym. J.* 1985, 17, 219.

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