

## A Kinetic Evidence for the Nitroxyl Radicals Recycling Mechanism in the Photostabilizing Process of HALS

Xiao Xuan LIU<sup>1,2\*</sup>, Xing Hong ZHANG<sup>1</sup>, Guang Guo WU<sup>1</sup>,  
Jian Wen YANG<sup>2</sup>, Zhao Hua ZENG<sup>2</sup>, Yong Lie CHEN<sup>2</sup>

<sup>1</sup>Department of Chemistry, Shantou University, Shantou 515063

<sup>2</sup>Institute of Polymer Science, Zhongshan University, Guangzhou 510275

**Abstract:** The photoinduced bulk polymerization of a reactive-hindered amine light stabilizers (r-HALS), 4-acryloyl-2, 2, 6, 6-tetramethylpiperidiny (ATMP), was performed at 80 °C by using a DPC technique. An unique periodic exponential attenuation-type oscillating curve was found when the polymerization was carried out in air, but this phenomenon was not found in nitrogen. It is supposed that this unique kinetic performance may be attributed to nitroxyl radicals that are produced *in situ* from the oxidation of ATMP. ATMP polymer with narrow polydispersity ( $d = 1.03$ ) can be obtained by photoinduced solution polymerization of ATMP. The signal detected in ESR may be assigned to the nitroxyl radicals in the matrix of ATMP polymer. Since this kind of recycling of nitroxyl radicals is well documented for the photostabilizing mechanism of HALS, the present results may serve as a kinetic evidence for this mechanism.

**Keywords:** Photopolymerization kinetics, reactive-HALS (r-HALS), periodic exponential attenuation-type oscillating cycle, photostabilizing mechanism, nitroxyl radicals ( $>N-O\cdot$ ).

The most commonly invoked photostabilizing mechanism of HALS involves scavenging of free radicals by HALS, it have been the subject of much research over the past 30 years<sup>1</sup>. Bauer *et al.*<sup>2</sup> have summarized the nitroxyl radicals recycling mechanism of photostabilization. In this recycling, amine group ( $>N-R$ ) of the piperidine ring in HALS structure is oxidized to nitroxyl radicals ( $>N-O\cdot$ ), which in turn react with alkyl radicals or acryloxy radicals to produce the derivatives of HALS ( $>N-OR$  or  $>N-CO-R$ ). Most of the recycling mechanism ever reported were based on theoretical reasoning, there were some reports on the *real-time* monitoring the concentration of  $>N-O\cdot$  in the photoaging process of polymers. The experimental kinetic evidences have been lacking in this field, which led to the contention on the photostabilizing mechanism of HALS among different schools in science for a long time. In our previous work<sup>3,4</sup>, we have synthesized and characterized a series of reactive HALS (r-HALS), as a polymerizable HALS monomer, whose reactivity and kinetics of photopolymerization and photostabilizing performances applied in UV-curing coatings were reported. In this paper, a new kinetic performance of unique periodic oscillating was found. We have prepared ATMP polymer that was characterized by ESR and GPC.

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\* E-mail: xxliu@stu.edu.cn

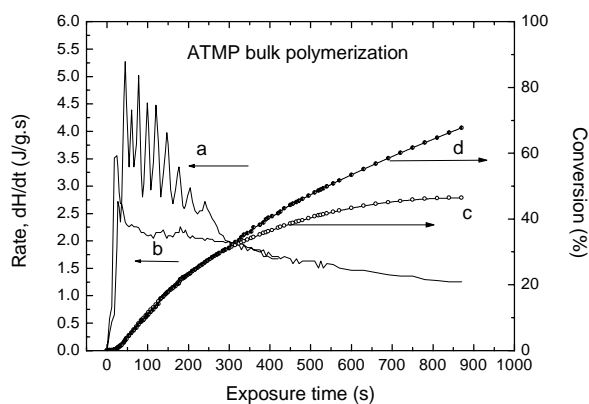
## Experimental

ATMP (4-acryloyl-2, 2, 6, 6-tetramethylpiperidiny) was prepared in our lab<sup>3</sup>. The photoinduced bulk polymerization of ATMP was performed at 80 °C by using a differential photocalorimeter (DPC). Darocur1173 (2, 2-dimethyl-2-hydroxy-acetophenone, from Ciba) as a initiator. The reactant mixture of ATMP (8.00~10.00 mg) and Darocur1173 (3.55 wt%) were accurately weighed as an irradiated sample. A modified CDR-1 DSC (made by Shanghai Balance Instrument Plant) was used to measure the exothermal rates of the samples. A medium pressure mercury lamp (300 W) as an irradiator embedded in a cooling water jacket made of quartz. The light intensity of the irradiation center was 2.54 mW/cm<sup>2</sup> measured by a UV-radiometer (type UV-A, made by Beijing Normal University Photoelectric Instrument Factory), which is sensitive in the wavelength range of 320~400 nm. Exothermal rates as a function of time were monitored under isothermal and continuous irradiation conditions by DPC technique<sup>5</sup>.

The photoinduced solution polymerization was carried out by the method of a plastic bag. ATMP (2.0~3.0 g) and Darocur1173 (2.0 wt%) were accurately weighed and dissolved in toluene. At ambient temperature, the reactant mixture was irradiated for a given exposure period. Finally, the ATMP polymer was separated and purified from the mixture by many times of precipitation with acetone/water. GPC analysis of the products using THF as an eluate at 1 mL/min was performed at 35°C on Waters 244 instrument equipped with Ustgragel-10<sup>3</sup> column and a Waters 410 RI detector (polystyrene was used as the standard). The ESR signals of nitroxyl radicals in the ATMP polymer were recorded on a JEOL TES-FEIXG ESR Spectrometer, the sensitivity is 10<sup>-6</sup> mol/L. ESR was performed at the condition of X-band standard cavity (center of field = 3385.00 G, scanning width = 100.00 G). The modulation amplitude was kept constant at 2.00 G and responding time 0.3 sec., the microwave power was held at 4 mW.

## Results and Discussion

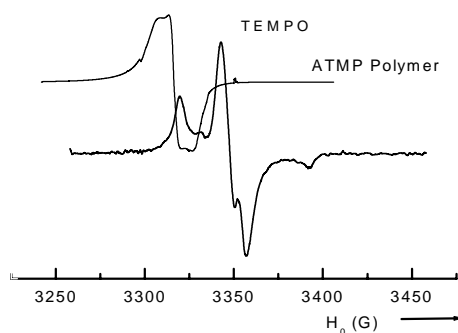
**Figure 1** The photopolymerization rate ( $dH/dt$ ) and the conversion vs. time plots for ATMP



Using Darocur1173 as a photoinitiator ([PI] content: 3.55 wt%), light intensity: 2.54 mW/cm<sup>2</sup>, 80°C, a, c line in air, b, d line in N<sub>2</sub>.

From **Figure 1**, a unique periodic oscillating curve was found when the polymerization was carried out in air (curve a), but this phenomenon was not found in nitrogen (curve b). It is supposed that this unique kinetic performance may be accounted for by the oxidation of ATMP into nitroxyl radicals that acts as a temporary terminator of the initiating (or propagating) radicals. Formed “dormant” species may decompose and the initiating (propagating) radicals regenerated. **Figure 1** also shows that the conversion of ATMP vs. time in nitrogen is obviously higher (curve d) than that in air (curve c) after the exposure time of 300 sec. It is in accordance with the result of our previous work<sup>6</sup>.

In the early stage, the initiator had been decomposed to generate a lot of primary radicals that reacted with ATMP monomer promptly, and the rate increased with the increase of concentration of primary radicals quickly. At the same time, >N-H of the piperidine ring had been rapidly transferring to >N-O<sup>•</sup> through induced oxidation by oxygen in air. When the concentration of >N-O<sup>•</sup> accumulated continuously and reached at the value of about  $10^{-6}$  mol/g which is the maximum value of its inhibition factor<sup>2</sup>, >N-O<sup>•</sup> began to capture promptly the propagating radicals to form “dormant” chain. Accordingly, the concentration of propagating radicals declined to lowest value and the rate decreased synchronously. Meanwhile the concentration of >N-O<sup>•</sup> also depleted to lose the quenching ability sharply, the first cycle of nitroxyl radicals from generation to “pseudo-dead” was accomplished. A new second cycle of nitroxyl radicals would begin after the propagating radicals are regenerated due to the continuing photolysis of initiator and the decomposition of “dormant”, and its concentration increased with the time. With the increase of time, the fate of >N-O<sup>•</sup> in the process may be described as: generation — capture (depletion) — generation again — capture (depletion) again ·····, therefore a periodic oscillating cycling kinetic phenomenon was realized. When the polymerization was proceeded in N<sub>2</sub> (curve b) there is no or very few >N-O<sup>•</sup> generated due to lack of oxygen, so the oscillating cycle cannot be found. The results have also indicated that the cycle curve is in exponential attenuation during the progress of polymerization. The generation of >N-O<sup>•</sup> *in situ* in the system above is the key factor causing the oscillating kinetic cycle. If >N-O<sup>•</sup> was generated and bound onto the polymer chains, ESR signals of >N-O<sup>•</sup> would be detected in ATMP polymer. In order to verify that new conception stable nitroxyl radicals would be generated *in situ* when ATMP is photopolymerized, the ESR signals monitored in the process were as shown in **Figure 2**. The ESR signals of nitroxyl radicals obtained from the solid powder of ATMP polymer was not exactly the same as that in solution state which is a well-resolved triplet. The nitroxyl radicals are bonded onto the polymer matrix, it is considered that the structural restriction results in the broadening of the ESR signals<sup>7</sup>. This is due to the influence of superfine splitting factor  $\alpha$  ( $\alpha_1$ ,  $\alpha_0$  and  $\alpha_{+1}$  is 34.94, 15.97 and 22.07 G, respectively) and interference of a few of nitroxyl radicals which capped the end of polymer chain. The value of the factor  $\alpha_0$  of ATMP polymer is in accordance with  $\alpha_0$  of TEMPO in methanol (16.05 G)<sup>8</sup>. The molecular weights of the ATMP polymer ( $\bar{M}_n = 27390$  and  $\bar{M}_w = 28413$ ) as well as polydispersity index ( $d = 1.03$ ) were determined by GPC. It is well known that the polymers with narrow polydispersity can be obtained by nitroxide-mediated “living” radical polymerization<sup>9</sup>, the results is another indication for the generation of nitroxyl radicals *in situ*.

**Figure 2** ESR first derivative spectra of TEMPO and ATMP polymer

The ESR signals for TEMPO and ATMP polymer were amplified to 2.5 and 2500 times, respectively.

### Conclusion

A unique periodic exponential attenuation-type oscillating phenomenon was found in the photopolymerization of ATMP in the air. ESR signals of nitroxyl radicals have been detected in the ATMP polymer with a narrow polydispersity of 1.03. The *in situ* generation of nitroxyl radicals during the process is confirmed and present results are considered as a kinetic evidence of nitroxyl radicals recycling mechanism in the photostabilization of HALS.

### Acknowledgments

Authors thanks to the National Natural Science Foundation of China (No.20274023), key project foundation of National Ministry of Education (No.02114) and Guangdong Province Natural Science Foundation of China (No.021241) for supporting this work.

### References

1. X. Liu, Y. Chen, *Gaofenzitongbao (Polymer Bulletin, in Chinese)*, **1999**, 4, 57.
2. D. R. Bauer, J. L. Gerlock, D. F. Mielewski, *Polym. Deg. Stab.*, **1990**, 28, 115.
3. X. Liu, J. Yang, Y. Chen, *Polym. Adv. Technol.*, **2002**, 13 (3-4), 247.
4. X. Liu, J. Yang, J. Huang, and Y. Chen, *Gongnenggaofenzixuebao (Journal of Functional Polymers, in Chinese)*, **2001**, 14 (4), 387.
5. Y. Chen, M. Zheng, Z. Liang, *Yingyonghuaxue (Applied Chemistry, in Chinese)*, **1994**, 11 (2), 27.
6. X. Liu, G. Wu, Y. Chen, J. Yang, Z. Zeng, Y. Chen, *Chemical Research in Chinese Universities*, **2002**, 18 (3), 159.
7. J. L. Gerlock, D. F. Mielewski, D. R. Bauer, *Polym. Degrad. Stab.*, **1988**, 20, 123.
8. K. Wang, Q. Luo, X. Zhou, *Advanced Instrument Analysis for Polymers*, first edition, Tsinghua University press, **1991**, p.71.
9. H. P. N. Veregin, M. K. Georges *et al.*, *Macromolecules*, **1995**, 28, 4391.

Received 14 October, 2002