RAFT 剤の置換基が光重合開始ラジカルとの反応に及ぼす影響の検証

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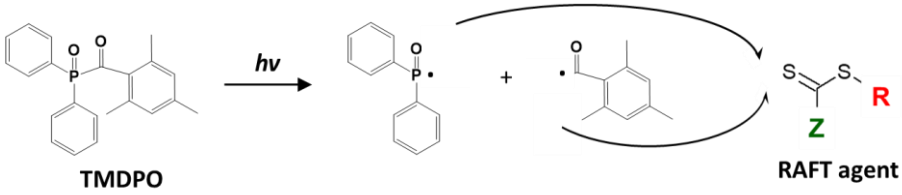
Verification of the effect of substituents in RAFT agents on their reaction with photo-initiated radicals (*Faculty of Molecular Chemistry and Engineering*, *Kyoto Institute of Technology*) ○ Yusuke Miyake, Takahiro Iwami, Kaho Tanabe, Kenji Kanaori

Reversible addition-fragmentation chain transfer (RAFT) polymerization, a type of living radical polymerization, enables simple and precise polymer design and reaction control only by adding a RAFT agent. Self-assembly formation under control of temperature further could expand the design of functional polymers, and the use of photoinduced initiation reactions is required. In this study, we focused on the photo-polymerization initiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO), which has been reported to realize efficient and relatively highly controllable polymerization. Reaction mechanism and reactivity between the radicals generated from TMDPO and RAFT agents with different structural characteristics were evaluated using electron spin resonance (ESR) spectroscopy, and the possibility of side reactions in the use of TMDPO were discussed. The structure of the reaction intermediate radical species observed by ESR spectroscopy differed depending on the structure of the RAFT agents. Furthermore, the reactivity between benzoyl radicals and RAFT agents showed particularly significant differences depending on the structure of the RAFT agents. They suggested the influence of the structural characteristics of the RAFT agent on side reactions.
Keywords : Photo-initiator; RAFT agent; ESR spectroscopy; Radical reaction mechanism

リビングラジカル重合法の一種である可逆的付加開裂連鎖移動（RAFT）重合法は RAFT 剤添加により簡易かつ精密な高分子設計と反応制御を実現する。自己集合体形成は更なる機能性ポリマーのデザイン性を更に広げるが、温度コントロールが重要となり、光誘起開始反応の利用が求められる。[1] 本研究では効率的かつ比較的制御性の高い重合の実現例が報告される光重合開始剤 Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide (TMDPO)に着目した。開始剤より生じるラジカルと、構造的特徴の異なる RAFT 剤との反応性および反応機構について、電子スピン共鳴（ESR）分光法により評価し、TMDPO 利用における副反応の可能性および RAFT 剤の構造的特徴との相関性の検証を行った。ESR 分光法により観測された反応中間体ラジカル種の構造と、TMDPO より生じるベンゾイルラジカルとの反応性において特に顕著な差が見られ、RAFT 剤の構造的特徴が副反応に及ぼす影響が示唆された。



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