ラジカル重合を用いる多分岐高分子の制御合成における分岐モノ マーの実用的合成

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Practical Synthesis of Branch-inducing Monomers for the Radical-mediated Synthesis of Structurally Controlled Hyperbranched Polymers (¹*Institute for Chemical Research, Kyoto University*) OJin Suzuki, ¹ Masatoshi Tosaka, ¹ Shigeru Yamago, ¹

We have already succeeded in the synthesis of hyperbranched polymers (HBPs) with controlled structure, not only for molecular weight and dispersity but also branch numbers and branch density, by the copolymerization of vinyl telluride 1 under organotellurium-mediated radical polymerization (TERP) (Eq. 1). However, there are still challenges with the synthesis and the optimization of the physical properties of 1. For example, 1a (R = Me), which was reported for our first paper, was obtained only in low yield due to a low boiling point. Furthermore, it could not be used in emulsion polymerization in water. In addition, it is difficult to experimentally confirm its introduction into the polymer chain. On the other hand, 1b ($R = C_2H_4Ph$) is advantageous to confirm its introduction into the polymer chain using the characteristic features of the Ph group, but the synthetic yield of 2b was also low due to its high boiling point. In this study, we synthesized 1 with various R groups to increase its synthetic efficiency and also investigated the effect of R group in the HBP synthesis.

Keywords: Hyperbranched polymer, Organotellurium-mediated radical polymerization, Vinyl telluride, Controlled polymerization, Tellurium

我々は既に有機テルル化合物を用いたラジカル重合(TERP) において、ビニルテルリド 1との共重合により、分子量と分散度と共に、分岐数や分岐密度といった分岐構造を制御して多分岐ポリマー(Hyper branched polymer, HBP)を合成することに成功している(式 1) 2。しかし、1 の合成や物性については必ずしも満足するものではない。すなわち、最初に報告した 1a (R=Me) は沸点が低いために合成収率が低いと共に 2a、エマルジョン重合においては水と相分離してしまう 2b。また、1 の高分子鎖への導入を直接確認することも難しい。一方、1b ($R=C_2H_4Ph$) は Ph 基の特長を利用して高分子鎖への導入を確認できる 2b。しかし、沸点が高いために合成収率は低かった。本研究では、これらの問題の解決のため、種々の R 基を持つ 1 を合成し、その合成効率と、1b を 1b を 1

$$\begin{array}{c} \text{CO}_2\text{Et} \\ \text{Te Me} \end{array} + \begin{array}{c} \text{R} \\ \text{Te Me} \end{array} + \begin{array}{c} \text{CO}_2\text{Me} \\ \text{60 °C} \end{array} \qquad \begin{array}{c} \text{AIBN} \\ \text{60 °C} \end{array} \qquad \begin{array}{c} \text{CO}_2\text{Et E} \\ \text{R} \\ \text{I} \end{array} \qquad \begin{array}{c} \text{Te Me} \\ \text{E = CO}_2\text{Me} \end{array} \qquad (1)$$

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