

§8. Polyester Synthesis by Microwave Assisted Rapid Polycondensation

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Currently, because of increasing concerns about damage to the environment, the development of new, eco-friendly (industrially related) chemical reactions and materials is important. Consequently, aliphatic polyesters have attracted much interest as environmentally benign and biodegradable polymers. We reported that at or near room temperature direct polycondensations of diols and dicarboxylic acids, catalyzed by rare-earth metal with electron-withdrawing ligands afford aliphatic polyesters with number average molecular weights (M_n) $>10^4$ (room-temperature polycondensation¹⁾), although polyesters are commercially produced by polycondensation under severe condition (at a high temperature and under an extremely reduced pressure).

Rapid syntheses that depend on microwave irradiation have also attracted interest because they are environmentally benign. Microwave irradiation has been used to shorten the reaction times of organic syntheses, to decrease the levels of side products, and to improve the yields and/or chemoselectivities of the products²⁾. Previously, we have demonstrated that dehydration polycondensations of various dicarboxylic acids and 3-methyl-1,5-pentanediol (MPD) catalyzed by $\text{Sc}(\text{OTf})_3$ under the condition of a moderate temperature were accelerated using the multimode microwave heating (2.45 GHz, up to 200W) compared with the conventional heating. In this report, we investigated about the acceleration of dehydration polycondensations using single-mode microwave reactor.

First, we investigated that the polycondensation was accelerated by the irradiation of electric and magnetic field. MPD (0.83 g, 7.0 mmol), adipic acid (1.02 g, 7.0 mmol), and scandium trifluoromethanesulfonate (6.9 mg, 1.4×10^{-5} mol) in quartz test tube were mixed at 80 °C until a homogeneous state was observed. The homogeneous sample was set into a single-mode microwave reactor. Electric or magnetic field irradiated the reaction mixture. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of each polyester was estimated using a size exclusion chromatography (SEC) system.

When 10W electric field was irradiated, the polycondensation was accelerated (Fig. 1, left). However, when 20 ~ 40W electric field was irradiated, decomposition of polyester by heat was induced. Similarly, when 20,40W magnetic field was irradiated, the polycondensation was accelerated, but when 60,80W magnetic field was irradiated, decomposition of polyester by heat occurred (Fig. 1, right).

Next, to investigate the effect of the substrates, the polycondensation of MPD and various dicarboxylic acids (succinic acid, adipic acid, sebacic acid) irradiated by electric field (10W) and magnetic field (40W). In the case of electric field, polycondensations of MPD and each dicarboxylic acid proceeded (Fig. 2, left), but in the case of magnetic field, polycondensations of MPD and adipic acid only proceeded (Fig. 2, right). These results showed that the relationship between magnetic field and substrates influences the polycondensation behavior.

In summary, we demonstrated that microwave heating accelerates the rate of AdA/MPD polycondensation catalyzed by $\text{Sc}(\text{OTf})_3$ at a moderate temperature and that a smaller amount of catalyst can be used than in a conventional polycondensation. These fundamental results in this report provide new guidelines for microwave-assisted, eco-friendly material design.

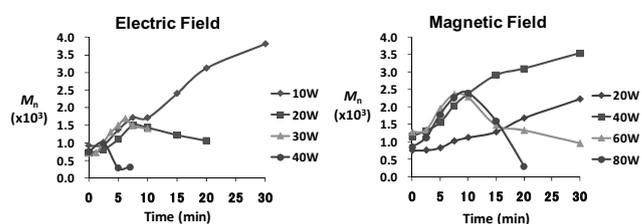


Fig. 1. Plots of M_n vs. time for the polycondensation of adipic acid and 3-methyl-1,5-pentanediol using electric field irradiation (left) and magnetic field irradiation (right).

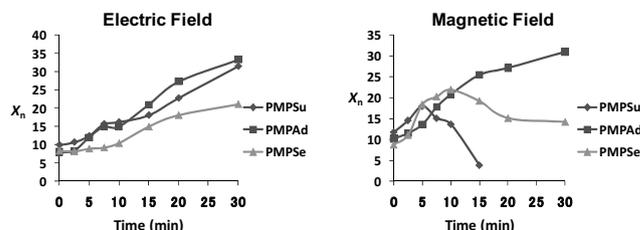


Fig. 2. Plots of M_n vs. time for polycondensations of 3-methyl-1,5-pentanediol and various dicarboxylic acids [blue : succinic acid, red : adipic acid, green : sebacic acid] using electric field irradiation (left) and magnetic field irradiation (right).

- 1) (a) A.Takasu et al. : *Macromolecules* **2003**, 36, 1772.
(b) A.Takasu et al. : *Macromolecules* **2005**, 38, 1048.
(c) A.Takasu et al. : *Macromolecules*. **2010**, 43, 144.
- 2) C.O.Kappe, *Angew. Chem. Int. Ed.* **2004**, 43, 6250.