

# Development of High-Performance and Specific Functional Bioplastic Materials from Biomass Resources

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## **Abstract**

Many research groups have investigated various chemical reactions to give useful chemical compounds from biomass resources,<sup>1,2)</sup> because it is important for the carbon neutral concept in chemical industry.<sup>3,4)</sup> On the other hand, it is desirable to develop new synthetic methods of high-performance polymer materials such as petroleum plastics from biomass feedstock in polymer industries. Therefore, we focus on the development of new high-performance and specific functional bioplastic materials from biomass resources. Acrylic resins are particularly important polymer materials synthesized from petroleum chemicals. In the past decade, the synthesis of bio-based acrylic resins from biomass feedstock and its derivatives, such as sugar, cellulose, and lignin, has been studied. However, such syntheses from these resources are very difficult.

Poly(hydroxyalkanoate)s (PHAs) are a family of bio-based aliphatic polyesters synthesized by bacteria from biomass resources; they produce unsaturated carboxylic acid as an olefin monomer under thermal degradation at high temperatures.<sup>5)</sup> As an example, the pyrolysis of poly(3-hydroxybutyrate) (P3HB) yields crotonic acid as a major product.<sup>6,7)</sup> On the other hand, cinnamic monomers are aromatic compounds that can be extracted from certain plants, such as *Cinnamomum cassia*, and derived by thermal decomposition of lignin, a complex phenolic biopolymer comprising wood or straw fiber cell walls along with cellulose.<sup>8-10)</sup> Characteristically, these compounds have an aliphatic or an aromatic substituent at the  $\beta$ -position of  $\alpha,\beta$ -unsaturated carbonyl groups likely acrylic monomers. Therefore, we focus on crotonic acid, cinnamic acid and these derivatives as monomers. However, these compounds are not easily polymerized. In fact, alkyl crotonates and alkyl cinnamates cannot be polymerized by the common radical initiators such as azobisisobutyronitrile (AIBN).

Recently, we found that some organic strong acids catalyzed the group-transfer polymerization (GTP) of  $\beta$ -substituted- $\alpha,\beta$ -unsaturated carboxylates such as alkyl crotonates and alkyl cinnamates.<sup>11,12)</sup> Linear alkyl crotonates such as ethyl crotonate (EtCr), *n*-propyl crotonate (<sup>*n*</sup>PrCr) and *n*-butyl crotonate (<sup>*n*</sup>BuCr) were smoothly polymerized to give the corresponding polymers in good yields (72%, 99% and 64%) for 24 hours at  $-40$  °C. However, as the steric hindrance of alkyl ester groups became higher, the yields of the obtained poly(alkyl crotonate)s (PRCr) were decreased. *tert*-Butyl crotonate (<sup>*t*</sup>BuCr) could not polymerized by this system. On the other hand, to obtain higher molecular weight of PRCr suitable for physical properties, the polymerization was conducted at a feed ratio Monomer/Initiator/Catalyst of 400/1/0.2 under otherwise identical conditions. Alkyl crotonates (methyl crotonate (MeCr), EtCr, <sup>*n*</sup>PrCr, isopropyl crotonate (<sup>*i*</sup>PrCr), <sup>*n*</sup>BuCr, secondarybutyl crotonate (<sup>*s*</sup>BuCr), and isobutyl crotonate (<sup>*i*</sup>BuCr)) were successfully polymerized to give the obtained polymers with highly molecular weight from  $3.0 \times 10^4$  to  $7.2 \times 10^4$  g/mol. The thermal stabilities of the PRCr obtained by organic acid-catalyzed GTP were generally superior to those of poly(alkyl methacrylate)s. The values of the total light transmittance ( $T_t$ ) and haze of the PRCr films were similar to those of both PMMA films and glass plates.

Cinnamates were also successfully polymerized by the GTP technique through the general GTP mechanism. The obtained polymers exhibited high thermal stabilities comparable to and even exceeding those of engineering plastics. The structural analyses clearly revealed that the poly(alkyl cinnamate)s and derivatives synthesized using the GTP system have substituents at both the  $\alpha$ -position and the  $\beta$ -position in the main chain, which is expected to decrease the flexibility of the main chain. The increase in stiffness derived from the decrease in flexibility might have a considerable effect on the high thermal stability. Herein, I show more details of my research and also show the syntheses of various types of bioplastics in Bioplastic Research Team (RIKEN).

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