

Creation of New Reactions of Oxetanes and Their Application to Polymer Synthesis

Tadatomi Nishikubo and Hiroto Kudo

Department of Applied Chemistry, Faculty of Engineering, Kanagawa University,
3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686 Japan
nishikubot@kanagawa-u.ac.jp

1. INTRODUCTION

4-Membered cyclic ethers, oxetanes have high strain energy (107 kJ/mol) as 3-membered cyclic ethers, oxiranes, and the former ethers have higher basicity than the latter ones. Furthermore, it is well known that the cationic ring opening polymerization of oxetanes proceeds¹ very smoothly with suitable catalysts to afford the corresponding poly(ether)s. The first commercial polymer from oxetane is poly[(3,3-bis(chloromethyl)oxetane)] (PENTON[®]) from Hercules, which was prepared by the ring-opening polymerization of (3,3-bis(chloromethyl)oxetane) (BCMO). More than 10 years ago, Crivello et al reported² photoinitiated cationic ring-opening polymerization of oxetanes using certain photo-acid generators. This reaction system is very important technology³ for UV-curing field, because this reaction system has good characteristic properties such as high curing speed, good adhesion to substrates, and low volume shrinkage after UV-curing compared with oxiranes.

However, any other useful organic reaction of oxetane compounds excepting the cationic ring-opening polymerization has not been reported, although many useful organic reactions of oxiranes such as cationic- and anionic ring-opening polymerizations, anionic alternating ring-opening polymerization, and many ring-opening addition reactions with certain reagents such as amines, carboxylic acids, phenols, thiols, acyl halides, silyl chlorides, phosphonyl chlorides, active esters, aryl phosphonates, and aryl silyl ethers have been reported, and these reaction systems of oxiranes have been widely used in industry.

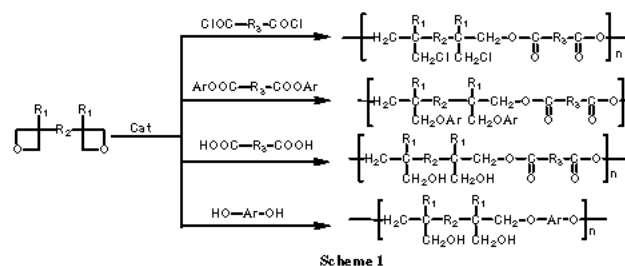
From these backgrounds, about 15 years ago, I was interested in developing new reactions of oxetanes, and successfully found⁴⁻⁶ certain new ring-opening addition reactions of oxetanes with acyl chlorides^{7,8}, active esters⁹, thio esters¹⁰, silyl chlorides¹¹, and phosphonyl chlorides¹². These reactions can be applied to the polymer synthesis. We also examined the development of further new ring-opening addition reactions of oxetanes with phenols¹³, thiols¹⁴, carboxylic acids¹⁵, and phosphonic acids. More recently, we succeeded¹⁶ in developing novel anionic ring-opening polymerization of (3-hydroxymethyl)oxetanes using potassium *tert*-butoxide and 18-crown-6-ether complex as a catalyst and anionic ring-opening alternating copolymerization of oxetanes¹⁷ with cyclic dicarboxylic anhydrides using appropriate quaternary onium salts as catalysts. All these reactions proceed very smoothly to give the corresponding adducts and polymers in high yields.

2. RESULTS AND DISCUSSION

The polyaddition of bis(oxetane)s with di(acyl chloride)s proceeded⁷ very smoothly at 90 °C to give the corresponding reactive polyesters containing pendant chloromethyl groups using certain quaternary onium salts as catalysts (**Scheme 1**). The resulting poly(ester)s have been used as starting polymers for the synthesis of functional polymers. The polyaddition of bis(oxetane)s with di(thio ester)s proceeded¹⁰ very smoothly at higher temperatures than 150 °C using appropriate catalyst such as tetraphenylphosphonium bromide

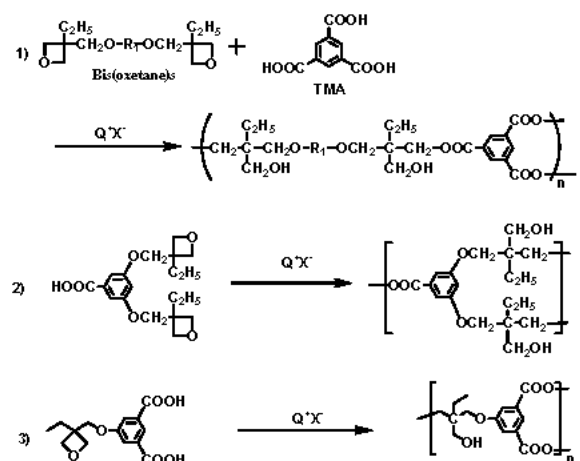
(TPPB) to produce high molecular weight polyesters. The polyaddition of bis(oxetane)s with di(active ester)s of bis(phenol)s produced corresponding polyethers.

Polyadditions of bis(oxetane)s with di(carboxylic acid)s¹⁵ and bis(phenol)s¹³ did not occur under 110 °C at all. However, these polyadditions proceeded smoothly at higher temperature than 150 °C. This means that these reactions can be applied to new thermo-setting resin^{13a} with a single-component at room temperature. Further advantage of these reactions is that the produced primary hydroxy groups do not react essentially with the oxetane groups under the normal conditions employed. This is unlike the reaction of epoxy compounds with carboxylic acids or phenols, and is important in terms of reaction control in the synthesis of linear polymers or modification of reactive side chains.



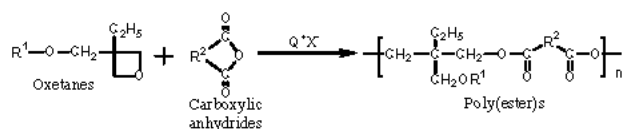
Scheme 1

We also prepared¹⁸ hyperbranched polyesters with pendant hydroxy groups by the polyaddition of A₂ monomers with B₃ monomers, or by the self-polyadditions of A₂B₂ or A₂B type monomers (**Scheme 2**).



Scheme 2

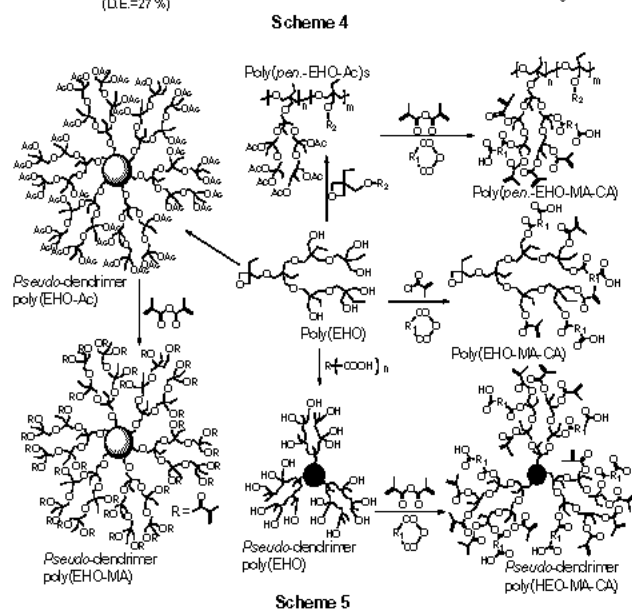
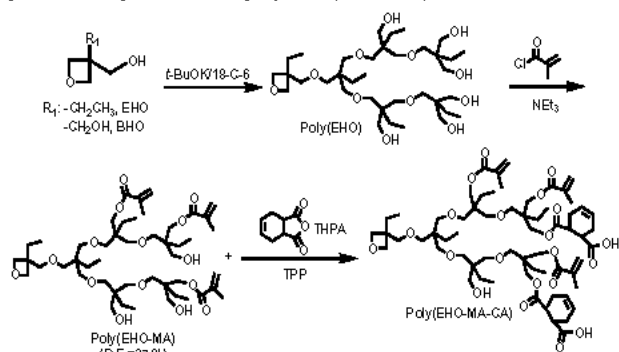
The anionic alternating ring-opening copolymerization of certain oxetane monomers with cyclic carboxylic anhydrides proceeded¹⁷ smoothly at 130 °C using quaternary onium salts or crown ether complexes as catalysts to form corresponding polyesters (**Scheme 3**), and it was found that the resulting polyester shows the highest *M_n* and yield, when the reaction is performed with equivalent molar ratio of oxetane and carboxylic anhydride.



Scheme 3

The anionic ring-opening polymerization of (3-ethyl-3-hydroxymethyl)oxetane (EHO) proceeded¹⁶ at higher temperatures than 120 °C, and the yields and *M_n*s of the polymers increased with reaction temperatures. It was also found that the obtained polymer [poly(EHO)] had one terminal oxetane group and many pendant hydroxy groups as shown in **Scheme 4**. Therefore, the resulting poly(EHO) has been used as a starting material for the synthesis of hyperbranched photo-curable poly(ether) containing terminal methacryloyl groups (poly(EHO-MA)) and alkaline developable photo-curable poly(ether) both containing terminal methacryloyl groups and carboxyl groups (**Scheme 4**). The anionic polymerization of 3,3-bis(hydroxymethyl)oxetane (BHO) also proceeded smoothly to give the corresponding poly(BHO) under the same conditions.

Furthermore, the resulting poly(EHO) has been used¹⁹⁻²¹ as a starting material for the synthesis of *pseudo*-polydendron and *pseudo*-dendrimer. These *pseudo*-polydendron and *pseudo*-dendrimer have also been used as starting materials for the synthesis of high performance photo-curable polymers (**Scheme 5**).



3. CONCLUSION

We succeeded the synthesis of new functional polymers and oligomers by novel ring-opening addition reactions of oxetane compounds. We also examined the anionic ring-opening polymerization of EHO and BHO, and successfully synthesized corresponding hyperbranched poly(ether)s containing one oxetanyl group and many hydroxy groups in the end of polymer chains.

Furthermore, we successfully synthesized certain new photo-reactive *pseudo*-dendrimers and *pseudo*-poly(dendron)s containing many terminal (meth)acryloyl groups by the further chemical modification of the resulting poly(EHO).

4. REFERENCES AND NOTES

- [1] For example: Inoue, S.; Aida, T. "Ring-Opening Polymerization", Ivin, K. J. and Saegusa, T. Eds., Elsevier Applied Science Publishers: London, Vol. 1, pp. 185-298, **1984**.
- [2] Sasaki, H.; Crivello, J. V. *J. Macromol. Sci.*, **1992**, A29, 915.
- [3] (a) Sasaki, H.; Kuriyama, A.; Kakuchi, T. *Macromol. Rep.*, **1994**, A31, (Suppl. 5), 635. (b) Sasaki, H.; A. Kuriyama, A.; Kakuchi, T. *Macromol. Rep.*, **1995**, A32, 1699.
- [4] Nishikubo, T.; Sato, K. *Chem. Lett.*, **1991**, 697.
- [5] Sato, K.; Kameyama, A.; Nishikubo, T. *Macromolecules*, **1992**, 25, 1198.
- [6] For example; (a) Nishikubo, T.; Kameyama, A. *Kobunshi Kagaku*, **2003**, 52, 16. (b) Nishikubo, T.; Kameyama, A. *Chemistry and Chemical Industry*, **2004**, 57, 225. (c) Nishikubo, T.; Kudo, H. *J. Network Polymer, Jpn.*, **2006**, 27, 38.
- [7] (a) Kameyama, A.; Yamamoto, Y.; Nishikubo, T. *J. Polym. Sci. Part A: Polym. Chem.*, **1993**, 31, 1639. (b) Kameyama, A.; Yamamoto, Y.; Nishikubo, T. *Macromol. Chem. Phys.*, **1996**, 197, 1147.
- [8] Yashiro, T.; Saitou, T.; Kameyama, A.; Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.*, **2003**, 41, 2304.
- [9] Nishikubo, T.; Kudo, H.; Sasaki, M.; Kuwamura, K.; Imataki, C. *Polym. J.*, **2004**, 36, 841.
- [10] Kudo, H.; Kurakata, T.; Sasaki, M.; Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.*, **2004**, 42, 1528.
- [11] Minegishi, S.; Ito, M.; Kameyama, A.; Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.*, **2000**, 38, 2254.
- [12] Minegishi, S.; Tsutida, S.; Sasaki, M.; Kameyama, A.; Kudo, Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.*, **2002**, 40, 3835.
- [13] (a) Nishikubo, T.; Kameyama, A.; Ito, M.; Nakajima, T.; Miyazaki, H. *J. Polym. Sci. Part A. Polym. Chem.*, **1999**, 37, 2781. (b) Konno, Y.; Suzuki, H.; Kudo, H.; Kameyama, A.; Nishikubo, T. *Polym. J.*, **2004**, 36, 114. (c) Nishikubo, T.; Kudo, H.; Yoshihara, M.; Maruyama, K. *J. Polym. Sci. Part A. Polym. Chem.*, **2005**, 43, (10), 2028.
- [14] Nishikubo, T.; Kameyama, A.; Ito, M.; Suzuki, A.; *J. Polym. Sci. Part A. Polym. Chem.*, **1998**, 36, 2873.
- [15] Nishikubo, T.; Kameyama, A.; Suzuki, A. *Reactive & Functional Polymers*, **1998**, 37, 19.
- [16] (a) Kudo, H.; Morita, A.; Nishikubo, T. *Polym. J.*, **2003**, 35, 88. (b) Morita, A.; Kudo, H.; and Nishikubo, T. *Polym. J.*, **2004**, 36, 413. (c) Morita, A.; Kudo, H.; Nishikubo, T. *J. Polym. Sci. Part A. Polym. Chem.*, **2004**, 42, 3739.
- [17] Kameyama, A.; Ueda, K.; Kudo, H.; Nishikubo, T. *Macromolecules*, **2002**, 35, 3792.
- [18] (a) Nakagami, T.; Kudo, H.; Nishikubo, T. *Polym. Preprints, Jpn.*, **2003**, 52, 255. (b) Nakagami, T.; Iijima, E.; Kudo, H.; Nishikubo, T. *Polym. Preprints, Jpn.*, **2003**, 52, 254. (c) Nishikubo, T.; Kudo, H.; Nakagami, T. *Polym. J.*, **2006**, 38, 145. (d) Nishikubo, T.; Kudo, H.; Maruyama, K.; Nakagami, T.; Miyabe, H. *Polym. J.*, **2006**, 38, 447.
- [19] Morita, A.; Kudo, H.; Nishikubo, T. *Polym. Preprints, Jpn.*, **2003**, 52, 1453.
- [20] Morita, A.; Sugii, K.; Kudo, H.; Nishikubo, T. *Polym. Preprints, Jpn.*, **2004**, 53, 340.
- [21] Kudo, H.; Aoki, A.; Morita, A.; Nishikubo, T. *Polym. Preprints, Jpn.*, **2005**, 54, 1327.