Chemically Recyclable Vinyl Polymers Degradable to the Raw Materials via Pendant Hydrolysis

Yota Chiba, Faculty of Textile Science and Technology, Shinshu University
Yasuhiro Kohsaka, Research Initiative for Supra-Materials, Shinshu University;
Faculty of Textile Science and Technology, Shinshu University; JST PRESTO

Abstract

Chemical recycling of polymers to their monomers or precursors is a promising approach toward a sustainable society, although that of vinyl polymers remains challenging because of the chemically stable carbon main-chains. Herein, a new strategy for chemical recycling of vinyl polymers is proposed. The newly designed vinyl polymers underwent degradation into monomer precursors via the hydrolysis of their cyclic pendant groups. The degradation is irreversible and differs from the conventional approach to chemical recycling based on equilibrium control between the polymerization and depolymerization reverse reaction of polymerization.

Keywords: sustainable society, chemically recyclable vinyl polymer, cyclic vinyl monomer, hydrolysis

1. Introduction

To establish a sustainable society, reclamation of discarded materials is necessary. In particular, as polymer materials have caused environmental problems, including marine pollution, a model for resource circulation through thorough collection and recycling is strongly required.[1] The circulation of polymer materials is also important in terms of saving fossil resources, which are raw materials of synthetic plastics and fibers.

The recycling of polymer materials can be achieved through two different methodologies: mechanical recycling and chemical recycling. Mechanical recycling is a recycling process involving the melting and remolding of plastics.[2] This process has advantages in terms of energy consumption and economic cost.[3] However, mechanical recycling has fundamental issues such as an unavoidable quality decline due to decomposition at the molecular level and difficulty in its application to composite materials.[4] Chemical recycling is a process of renewing macromolecules by degrading polymers to monomers or their precursors and subsequent resynthesis.[5] Recycling at a molecular level guarantees the quality of recycled materials comparable to that of fresh products. Therefore, chemical recycling is an ideal process for sustainable resource circulation. A typical example of chemical recycling is that of poly(ethylene terephthalate) (PET), which reproduces the monomer by hydrolysis/alcoholysis of ester bonds.[6] An example of PET suggests that chemical recycling is promising for polymers consisting of 'weak' covalent bonds that are easily cleaved.[5]

Because vinyl polymers, prepared by addition polymerization of vinyl compounds, are the most widely produced plastics in the world,[7] their chemical recycling is highly desirable. However, the chemical recycling of vinyl polymers remains a challenge. Polyolefins such as polyethylene and polypropylene are composed of a stable carbon backbone that requires harsh conditions for cleavage.[8] In contrast, poly(methyl methacrylate) (PMMA) undergoes quantitative thermal decomposition to regenerate the monomer methyl methacrylate. This reaction progresses in a depolymerization mechanism, a reverse reaction of polymerization.[9] Although depolymerization reaction has a potential to realize resource circulation by chemical recycling, it includes some fundamental issues. For example, the reversible reaction system between polymerization and depolymerization means that monomers with high polymerizability give polymers with low depolymerizability.[9] To emphasize the depolymerization, the equilibrium must be controlled using harsh conditions such as high temperature, high dilution, and high vacuum. In addition, the generation of active species, typically radicals, is dependent on the structure of the polymer chain end, while free radical polymerization, which is widely used in industry, results in uncontrolled chain-end structures. Moreover, even if such issues are resolved, the depolymerization reaction may be accompanied by some side reactions. For these reasons, vinyl polymers that afford monomers quantitatively via depolymerization are limited to some exceptions, such as PMMA. An ideal scheme involves vinyl polymers that can be prepared by free radical polymerization and that can reproduce the monomers quantitatively by depolymerization. However, it is very difficult to achieve this using a reaction design based on a reversible system of polymerization and depolymerization.

We have proposed a new process for the chemical recycling of vinyl polymers, which is achieved by multistep reactions involving polymerization, degradation, and monomer regeneration. Herein, we report this concept and provide some recent examples.

2. Depolymerization of poly(styrene derivative)s triggered by hydrolysis of pendant groups

Recently, we reported the chemical recycling of vinyl polymers of **M1**, a cyclic styrene derivative (**Fig. 1A**).[10] This discovery was inspired by pioneering studies on α-substituted styrene monomers. Ito and Ueda reported the free radical polymerization of α-acetoxystyrene (**M2**) affording the corresponding vinyl polymer, **P2**, which underwent degradation by the treatment with a strong acid at 100 ℃.[11] This degradation reaction is composed of two steps: The protonation of the carbonyl pendants by an acid promoted the elimination reaction of acetic acid, and the generated tertiary benzyl cation initiate the cationic depolymerization. The depolymerization of **P2** is interesting in terms of chemical recycling. However, high depolymerizability implies low polymerizability. In fact, the ceiling temperature (T_c; polymerization and depolymerization proceed at equal rates at this temperature) of **M2** in a 1 M solution is 47 ℃. Because of this poor polymerizability, Ito and Ueda conducted free-radical polymerization of **M2** for 7–16 days to obtain **P2**.[12] Generally speaking, vinyl monomers with less steric hindrance around the vinyl group have higher T_c. Cyclic vinyl monomers, that is, α-exomethylene ring compounds, usually exhibit a higher T_c than the corresponding linear monomers because the cyclic structure restricts the possible conformations and reduces the steric hindrance around the vinyl (vinylidene) group. Hence, **M1**, the cyclic analog of **M2**, exhibits excellent polymerizability to afford **P1** with a high degree of polymerization under typical conditions of free radical polymerization.[12), 13] Our recent examination revealed that the T_c of **M1** was above 120 ℃.[10]

Unfortunately, treatment of **P1** with a strong acid did not induce depolymerization,[12] probably because of the stability of the five-membered lactone. We then examined the irreversible hydrolysis of the lactone pendants using a basic aqueous solution. **P1**, prepared by radical polymerization using 2,2′-azobisisobutyronitrile (AIBN), was treated with 1 M aqueous NaOH. in dimethyl sulfoxide (DMSO) at 70 ℃. **Fig. 1C** shows the changes in the ^{1}H NMR spectra of the reaction mixture before and after 30 min. The signals attributed to **P1** disappeared and a new set of signals assignable to the sodium salt of 2-acetylbenzoic acid (**R1**) was observed. The size-exclusion chromatogram (SEC) showed a decrease in the polymer peak and a growing peak in the sodium salt of **R1** (**Fig. 1D**). Herein, the degree of degradation, defined as the area ratio of the peak of the sodium salt of **R1** to the others, was 82% after 30 min. Neutralization of the reaction mixture by acid and extraction using dichloromethane yielded **R1** in 78% yield. Notably, chlorination of **R1** spontaneously followed intramolecular esterification to yield **M1**. Therefore, **M1** is chemically recyclable.

Fig. 1E shows the degree of degradation at each reaction time. The reaction at 70 ℃ resulted in almost complete degradation, while that at 25 ℃ was saturated at 50% degradation. **Fig. 1F** shows plots of the degree of degradation vs. number-averaged molar mass (M_n) of the polymer peaks in SEC. The linear relationship indicates a depolymerization mechanism during degradation. It should be noted that the y-intercept of the approximate line was approximately 1/2 of the initial M_n, suggesting that main-chain scission occurred at the earliest stage of the reaction. These analyses led to the reaction mechanism shown in **Fig. 2**. Since **M1** is a styrene derivative,

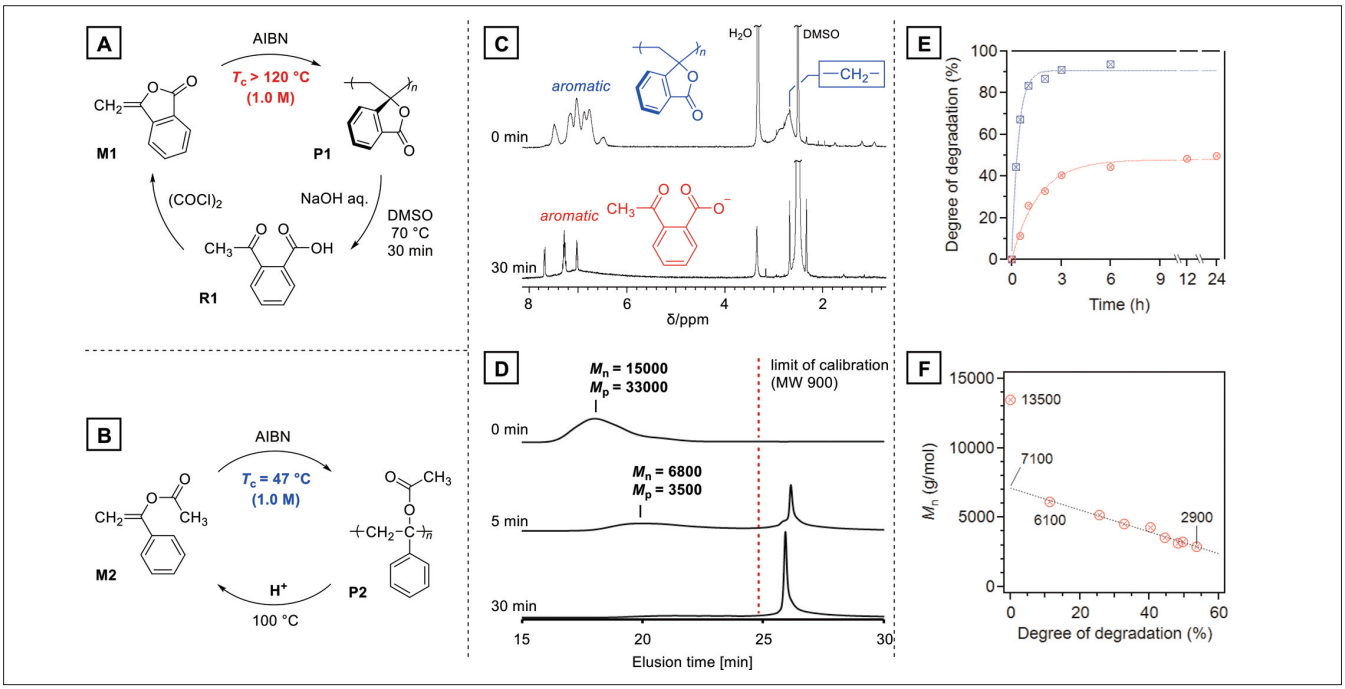

Fig. 1. **A**: Polymerization and chemical recycling of 3-methylene phthalide (**M1**). **B**: Radical polymerization and cationic depolymerization of α-acetoxystyrene. **C**: ^{1}H NMR spectra before and after the degradation of P2 (400 MHz, DMSO-d_6, 25 ℃). **D**: SEC profiles before and after degradation of **P1** (DMF, 40 ℃, polystyrene standard). **E**: Time growth of the degree of degradation of **P1** at 70 ℃ (blue squares) and 25 ℃ (red circles). **F**: Number-averaged molar mass (M_n) at each degree of P1 degradation.

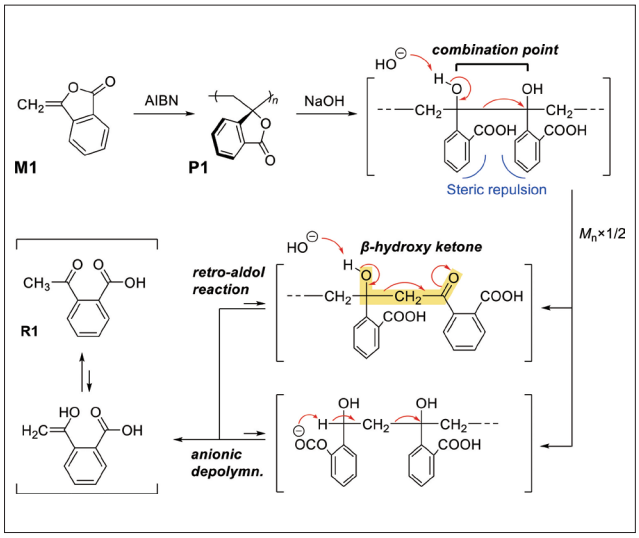

Fig. 2. Proposed degradation mechanism for **P1**.

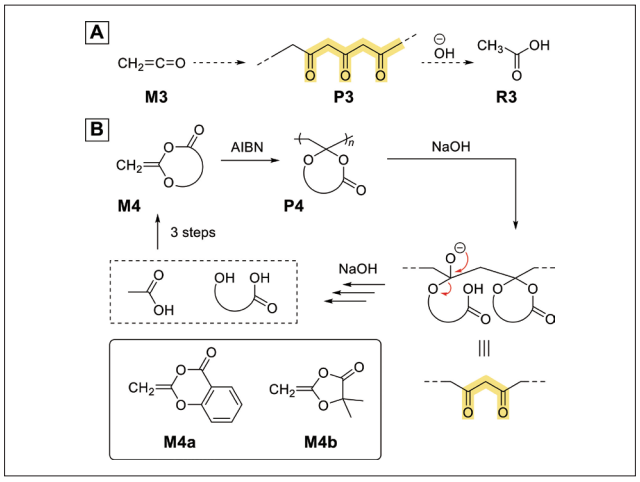

Fig. 3. A: Model polymer for chain scission via hydrolysis.
B: Chemically recyclable vinyl polymers of cyclic ketene acetal esters.

radical polymerization should be terminated mainly via a combination of radical species such as styrene.[14] The combination point, formed in the termination reaction, has the largest steric hindrance of pendant groups in the polymer chain, and chain scission should occur at the combination point. The base hydrolysis of lactone pendants of **P1** leads to ring opening, which emphasizes the steric hindrance of the pendant groups. As a result, main-chain scission occurs once at the combination point, followed by depolymerization. After careful investigation, we conclude that chain scission and depolymerization proceed via an anionic mechanism. One polymer-chain fragment containing a chain end of β-hydroxy ketone, the so-called aldol, results in depolymerization through the retro-aldol reaction, while another fragment undergoes anionic depolymerization. Both the depolymerization reactions afforded **R1**.

3. Chemical recycling of vinyl polymers via main-chain scission

In the previous section, we described the depolymerization from the chain-end using the retro-aldol reaction. This discovery gave the idea of carbon chain scission via reversed carbonyl condensation, such as the retro-aldol reaction and hydrolysis of 1,3-carbonyl compounds (retro-Claisen condensation). Therefore, **P3**, the simplest polymer containing 1,3-dicarbonyl skeletons in its repeating units, was expected to be degraded by hydrolysis. However, the corresponding monomer was ketene (**M3**), which is known to be unstable (**Fig. 3A**). Thus, **M4**, a synonym for **M3**, was investigated as an alternative monomer (**Fig. 3B**).

M4a, a vinyl compound derived from acetylsalicylic acid in two steps, is called as 'dehydroaspirin,' because its addition reaction with water yields acetylsalicylic acid.[15]The radical polymerization of **M4a** using AIBN afforded the corresponding vinyl polymer, **P4a** (M_n = 14500 g/mol, M_w/M_n = 1.49).[16), 17)] **P4a** was reacted with NaOH aq. in DMSO at 70 ℃, and the reaction was monitored using SEC and ^{1}H NMR spectrometry. The polymer signal in the SEC profile disappeared after 5 min, while the ^{1}H NMR spectrum after 1 h showed signals assignable to acetic acid and salicylic acid.[17)] The neutralization and extraction of the reaction mixture afforded salicylic acid in 99% yield. Since acetic acid and salicylic acid are raw materials for **M4a**, the monomer is chemically recyclable. **P4a** was also decomposed in an acidic solution, although the reaction was much slower than base hydrolysis.[16)]

Compared with depolymerization, chemical recycling based on main-chain scission described above has the disadvantage that an incomplete reaction results in oligomeric products and no recovery of the monomer or its precursors. Nonetheless, main-chain scission has advantages that differ from those of depolymerization. Because **P4** consists of a carbon backbone derived from acetic acid and pendant groups of hydroxycarboxylic acid, the molecular design shown in **Fig. 3B** can provide a wide variety of recyclable vinyl polymers with different pendant groups. Goto et al. reported **M4b** derived from 2-hydroxyisobutylic acid.[18)] Chemical recycling via main-chain scission is also applicable to copolymers with other vinyl monomers. A copolymer of **M4a** and vinyl acetate was treated with acidic water in DMSO, resulting in a decrease in molar mass. Because the homopolymer of vinyl acetate is not degradable, this result suggests that the degradability is given by **M4a**.

4. Perspective

Chemical recycling of polymer materials has become a modern trend in polymer science. Because resource circulation is an urgent issue, the research targets for recycling are mainly existing polymer materials. However, these polymers have not been developed for resource circulation, and their chemical recycling, particularly that of vinyl polymers, suffers from fundamental problems. Currently, the requirements for polymeric materials have changed, and the problems of existing technologies have been exposed; thus, it is essential to review the design of

molecules and reactions.

The strategy of chemical recycling, consisting of polymer degradation of the monomer precursors and reproduction of monomers from them, requires chemical conversion using highly active reagents. For the examples described here, the chlorination of carboxylic acid prior to intramolecular esterification is the key step to reactivate the decomposed stable product into reactive species. Chlorination is typically achieved using oxalyl dichloride, which is derived industrially from ethylene carbonate and chlorine. The raw materials of the former are ethylene, oxygen, and carbon dioxide, whereas the latter is produced by electrolysis of seawater. Consequently, carbon circulation using **M1** and **M4** can be achieved without fossil resources. We believe that such a design of molecules and reactions using sustainable resources will become a standard for future research and development of recyclable polymer materials.

●文　献

1) Environment Assembly of the United Nations Environment Programme, *"End plastic pollution: towards an international legally binding instrument."*, Nairobi, **2022**.
2) Schyns, Z. O. G.; Shaver, M. P. *Macromol. Rapid Commun.* **2021**, *42*, 2000415.
3) Uekert, T *et al. ACS Sustain. Chem. Eng.* **2023**, *11* (3), 965.
4) Zink, T.; Geyer, R. *J. Ind. Ecol.* **2019**, *23* (3), 541.
5) Worch, J. C.; Dove, A. P. *ACS Macro. Lett.* **2020**, *9* (11), 1494.
6) Suhaimi, N. A. S.; Muhamad, F.; Razak, N. A. A.; Zeimaran, E. *Polym. Eng. Sci.* **2022**, *62* (8), 2355.
7) Plastics Europe, *"Plastics – the fast Facts 2023"*, **2023**.
8) Soni, V. K.; Singh, G.; Vijayan, B. K.; Chopra, A.; Kapur, G. S.; Ramakumar, S. S. V. *Energy Fuels* **2021**, *35* (16), 12763.
9) Lohmann, V.; Jones, G. R.; Truong, N. P.; Anastasaki, A. *Chem. Sci.* **2024**, *15*, 832.
10) Chiba, Y.; Kawatani, R.; Kohsaka, Y. *ACS Macro Lett.* **2023**, *12* (12), 1672.
11) Ito, H.; Ueda, M., *J. Photopolym. Sci. Technol.* **1990**, *3* (3), 335.
12) Ito, H.; Ueda, M. *Macromolecules* **1990**, *23* (11), 2885.
13) Vinogradova, S. V.; Salazkin, S. N.; Korshak, V. V.; Chelidze, G.Sh.; Slonimskii, G.L. ; Askadskii, A.A.; Mzhel'skii, A.I. *Vysokomol. Soedin., Ser. A* **1970**, *12* (1), 205.
14) Zammit, M. D.; Davis, T. P.; Haddleton, D. M.; Suddaby, K. G. *Macromolecules* **1997**, *30* (7), 1915.
15) Babin, P.; Bennetau, B. *Tetrahedron Lett.* **2001**, *42*, 5231.
16) Kazama, A.; Kohsaka, Y. *Polym. Chem.* **2019**, *10* (22), 2764.
17) Kazama, A.; Kohsaka, Y. *Polym. Chem.* **2022**, *13* (47), 6484.
18) Oh, X. Y.; Ge, Y.; Goto, A. *Chem. Sci.* **2021**, *12* (40), 13546.

Yota Chiba
Ph D. candidate, Textile Technology Division, Department of Science and Technology, Graduate School of Medicine, Science and Technology, Shinshu University. JSPS Fellowship for Young Scientists (DC1).
Current research topic: Chemically recyclable vinyl polymers.

Yasuhiro Kohsaka
Associate Professor; Research Initiative for Supra-Materials (RISM), Interdisciplinary Cluster for Cutting Edge Research, Shinshu University. Faculty of Textile Science and Faculty of Textile Science and Technology, Shinshu University. JST PRESTO. Doctor of Engineering.
Biography: 2023–present Rising Star Researcher in Shinshu University; 2022–present JST PRESTO Researcher; 2018–present Associate Professor in Shinshu University; 2015 Tenure-Track Assistant Professor in Shinshu University; 2011 Assistant Professor in Osaka University; 2008 JSPS Fellowship for Young Scientists (DC1); 2011 Doctor of Engineering, Tokyo Institute of Technology. **Current research topic:** Polymer synthesis by monomer and polymerization designs.