DEPOLYMRIZATION OF POLYMERS IN IONIC LIQUIDS

Akio Kamimura[1,*], Shigehiro Yamamoto[1], Tomoki Okagawa[1], Tamami Otsuka[1] and Makoto Yoshimoto[1]

[1]Department of Applied Molecular Bioscience, Graduate School of Medicine, Yamaguchi University Ube 755-8611, Japan
e-mail: ak10@yamaguchi-u,ac,jp; TEL/FAX +81-836-85-9231

Abstract

Use of ionic liquids for the depolymerization of synthetic polymer was examined. Polyamides were readily converted into monomeric lactam in good yields and recovered ionic liquids were useful for iteration use. Polyamides were isolated by a direct distillation or an extraction from aqueous mixture. To accelerate the reaction, microwave irradiation was effective. For example, unsaturated polyester in fiber-reinforced plastics was readily depolymerized to give glass fiber and monomeric material under the conditions of microwave heating at 340 ºC. This improved method was successfully applied to not only synthetic plastics but also natural polymers for their conversion of monomeric materials.

Keywords: *ionic liquids, depolymerization, microwave irradiation, polyamides, FRP*

1. Introduction

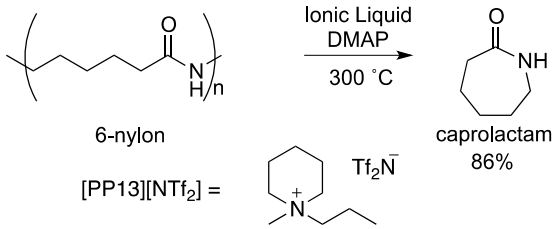
Conversion of plastics or polymers into monomeric material is recognized a key technology for achieving an effective chemical recycling. We have recently developed a new conversion for polymers into monomers using supercritical alcohols.[1] Although these methodologies provided useful and effective reactions, use of supercritical fluids always requires a high-pressure apparatus and special cares to treat them. Ionic liquids are a new type of solvent. They have interesting properties that have never been seen in any other organic solvents.[2] For example, they are less flammable by contacting with fire and non-volatile under very high temperature conditions. We were interested in these properties that would be very suitable for the depolymerization of polymers into monomers. Ionic liquids were usually ready for recycling use, and expected for using them several times in the same reaction. Thus, we started our investigation of using ionic liquids for the depolymerization of plastics and bio-derived polymers. Here we will show our recent developments on conversion of polymers into monomers using ionic liquids for achieving effective chemical recycling chemistry.

2. Materials and Methods

Ionic liquids were purchased from Kanto Kagaku Co. Ltd., Tokyo, Japan. The reactions were carried out in a usual glass apparatus. A glass tube oven or a sand bath was used for conventional heating of the reaction mixture. Microwave irradiation was achieved by using a microwave reactor made by Shikoku Keisoku, Japan. The reaction temperature was monitored and controlled by a thermo couple. All of monomeric products by the depolymerization reaction were isolated and checked by NMR and GC analyses. Ionic liquids were recovered and used for several times for the depolymerization reaction. The ionic liquids used for several times were purified by treatment with and alumina column and charcoal.

3. Results and Discussion

Depolymerization of polyamides was carried out in [PP13][NTf_2]. A mixture of nylon 6 and [PP13][NTf_2] was heated in a sand bath for 1 h at 300 ºC. Nylon 6 was dissolved in the ionic liquids and the reaction mixture became homogeneous black oil. Then the mixture was heated by a glass tube oven at 300 ºC for additional 6 h under reduced pressure. Caprolactam was isolated in pure form and [PP13][NTf_2] was recovered as a residue. The yield of caprolactam was 55%. The presence of catalytic amounts of DMAP (N,N-dimethylaminopyridine) promoted the reaction smoothly and the yield of the monomer was improved to 86% (Scheme 1).[3]

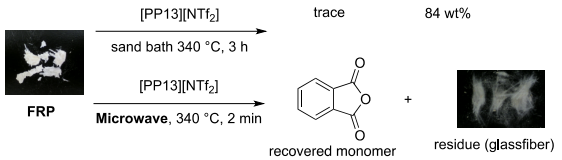


Scheme 1.

We examined a variety of ionic liquids and found that [PP13][NTf_2] gave the best results. The reaction progressed effectively at 300 ºC that was the most suitable reaction temperature; the depolymerization progressed in sufficiently when nylon 6 was treated under 300 ºC and higher reaction temperature provided side products such as N-methylcaprolactam. NMR charts of ionic liquids indicated that partial decomposition of [PP13][NTf_2] happened when the reaction was carried out under more than 300 ºC conditions. Recovered [PP13][NTf_2] was useful at least five times for the depolymerization reaction. The depolymerization reaction

of nylon 6 in modified ionic liquids were also examined.[4]

We next examined use of the microwave irradiation for the heating method for the depolymerization. Unsaturated polyester was widely used as a material for fiber-reinforced plastics (FRP), which is recognized as a most formidable plastic for the recycling. Treatment of FRP chips in ionic liquids at 340 ºC for 1 h in a sand bath failed the depolymerization and most of the starting FRP chip remained in its original shape. On the other hands, heating by microwave irradiation changed the reaction dramatically. Most of FRP chip dissolved in the ionic liquids and depolymerization progressed within 2 min of heating at 340 ºC. Glass fibers and phthalic anhydride, one of the monomeric materials of the unsaturated polyester, were recovered in good yields (Scheme 2).[5]

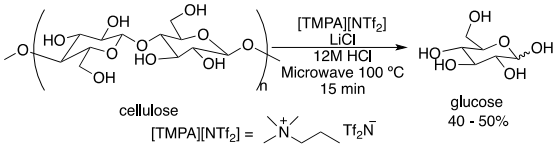


Scheme 2

[PP13][NTf_2] were recovered and used for several times for the depolymerization reaction. However, in this case non-volatile residue remained in the ionic liquids after the reaction. As a result the weight and the viscosity of [PP13][NTf_2] increased and their handling became not easy. We attempted their purification. The ionic liquids after several time uses in the depolymerization reaction were diluted with acetone and the resulting solution was passed through alumina column chromatography. Then the treatment of the solution with charcoal resulted in the decolorization of the ionic liquids. [PP13][NTf_2] were recovered in more than 90% and used for the depolymerization reaction again.

The microwave irradiation was also effective for the depolymerization of nylon 6. The reaction time was dramatically reduced and extraction work-up enabled to reduce energy consumption for the depolymerization reaction.

The present methodology was extended to the depolymerization of bio-derived polymers. For example, cellulose, massive amounts of which abandons in the world, is expected as a new chemical and energy sources today. We examined its depolymerization in ionic liquids. Although many efforts for the conversion of cellulose to monomeric materials in ionic liquids have been developed so far, most of the reports employ ionic liquids containing chloride anion in the anion part. However it is not easy to isolate glucose, one of the expected monomeric materials, from the reaction mixture because such ionic liquids are water-soluble. Use of hydrophobic ionic liquids would provide a good solution, but such ionic liquids do not solve cellulose.



Scheme 3

We used [TMPA][NTf_2] as the hydrophobic ionic liquids and examined LiCl and HCl as an additive for the reaction mixture. Use of HCl converted cellulose to glucose, but the yield was quite low. Combination use of LiCl and HCl in the reaction mixture improved the conversion. The optimal reaction temperature was 100 ºC and the microwave irradiation shortened the reaction time to 15 min. We finally succeeded to efficient conversion of cellulose to glucose in 40 – 50% yields when a large excess amount of LiCl was used.[6] As expected, glucose was readily isolated from the reaction mixture by simple extraction work-up. [TMPA][NTf_2] was also recovered and employed for iteration use. LiCl was also separated from glucose by treatment with acetone-iPrOH that solves only LiCl. The present method opens a new use of ionic liquids for feedstock recycling chemistry from biomass.

4. Conclusions

Ionic liquids were useful for the depolymerization of plastics. Their less flammable and non-volatile properties provide an easy depolymerization method for plastics. The depolymerization in ionic liquids was performed under normal pressure so that no special apparatus such as an autoclave is necessary. The less flammable property of ionic liquids reduces a risk of fire during the manipulation of the reaction. Ionic liquids are readily recovered and reused for several times. Although the prices of ionic liquids are relatively high at the moment, these properties will progress the more use of ionic liquids for the plastic recycling chemistry as well as the conversion of bio-resources for useful materials.

References

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