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Depolymerization of Nylon-66 by Hydrolysis Using Hydrophilic and Hydrophobic Ionic Liquid

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ABSTRACT

Ionic liquids have demonstrated potential efficiency as a catalyst in the hydrolysis technique for depolymerizing waste nylon-66. This research article involves the use of hydrophilic 1-butyl-3-methylimidazoliumtetrafloroborate [bmim]BF_4 and hydrophobic 1-butyl-3-methylimidazoliumhexafluorophospate [bmim]PF_6 ionic liquids for the breakdown of waste nylon-66. Hydrophilic ionic liquid has been demonstrated to be more efficient at catalyzing the hydrolysis of waste nylon-66 into monomers than hydrophobic ionic liquid. In experimental work, 0.2 g of waste nylon-66, 20 mL of 5 N HCl, and .01 mole ionic liquid were refluxed in the range of 100-140°C for several hours. After cooling, the reaction mixture was neutralized with 5N NaOH to make a slightly alkaline solution. The addition of benzoyl chloride to the alkaline solution gives the dibenzoyl derivative of hexamethylene diammine (DBHMD). The filtrate was extracted multiple times with ethyl acetate to obtain adipic acid. The ionic liquid was recovered at the end of the reaction under reduced pressure.

Keywords: Adipic acid, DBHMD, Depolymerization, Hydrophilic, Hydrophobic, Ionic liquid (IL).

INTRODUCTION

The production of synthetic textile fibers and filaments generates vast amounts of waste plastic in the environment. Due to the non-biodegradability of plastics leads to a several environmental problems. Plastic has a long-lasting nature and inexpensive production which lead to global waste management issues. The inappropriate disposal and accumulation threaten to the ecosystem, animals, and public health. The practice of disposing of waste plastic in landfills is widespread yet highly contentious. Plastics can cause environmental damage for hundreds of years in landfills because they are not biodegraded. Throwing away plastic waste in landfills not only takes up expensive space but also poses a major risk to the quality of soil and groundwater due to the possibility of dangerous chemicals seeping out[1]. Artificial polymer production uses finite, nonrenewable petroleum resources, which will soon be exhausted. These days, plastic is a necessary substance in our daily lives, and its widespread use has resulted in serious environmental problems. To combat the ecological crisis, conservation and the effective use and reuse of materials should be implemented. The depolymerization of waste

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plastic is a successful strategy for resolving these problems and promoting the sustainable growth of modern civilization. Through depolymerization, waste plastic is broken down into monomers, which can then be recycled into valuable goods and help to save natural carbon resources. There are so many methods that can employed for depolymerization including supercritical and subcritical fluids[2-3], pyrolysis[4] acid hydrolysis[5], catalytic[6-7], oxidative method[8-9] in which reaction conditions are relatively harsh. Biodegradation methods[10-11] are a further strategy for polymer breakdown in which microbes like Bacillus subtilis economically break down the polymer. However, due to adverse environmental conditions and long periods, some polymers can degrade using this method.

Ionic liquids have shown the potential to degrade the polymer into monomers. A special class of liquids known as ionic liquids is made up of only ions, and usually consists of an organic cation (phosphonium, ammonium, pyridinium, imidazolium, etc.) and an inorganic or organic anion (F-, Cl-, BF_4-, PF_6-F_3C-SO_3- etc.). These are the salts in liquid form with a melting point of less than 100°C or even room temperature (RTIL). Ionic liquid has some unique properties like low vapor pressure[12], high thermal stability[13], hydrophilic or hydrophobic[14], and adjustable physical and chemical properties[15]. Due to these reasons, ionic liquids have the potential to make a major contribution to the development of green chemistry and green technology.

Recently, there has been increased interest in ionic liquids due to their potential uses in recycling and waste management; one innovative type of ionic liquid that has been suggested for the chemical recycling of unsaturated polyesters and polyamides is soluble switchable ionic liquids or SILs. With the development of ionic liquids with solubility switches, liquid-liquid extraction of substances became easier to carry out[16]. Ionic liquids (ILs) have a major catalytic role in the breakdown of poly(ethylene terephthalate) (PET) by encouraging the cleavage of the C-O ester link, the pathway with the lowest barrier for PET glycolysis, which results in the creation of bis(hydroxyethyl)terephthalate (BHET) monomers[17]. A [Bmim][BF_4] catalyst was used to depolymerize PET in supercritical ethanol. In 45 min, this approach recovers 98 weight percent of diethylterephthalate[18].

Regarding the depolymerization of waste plastics using ionic liquids, there are a few possible gaps in the literature that need to be filled. The use of ionic liquids to depolymerize particular plastic kinds, like polyester or PET, has been extensively studied. However, there might not be enough information in the literature about employing imidazolium-based ionic liquids like [bmim]BF_4 and [bmim]PF_6 to depolymerize polyamides like nylon-66 into their monomers. The proposed study aims to investigate the use and the comparative study of hydrophilic [bmim] BF_4 and hydrophobic [bmim]PF_6 ionic liquids to degrade synthetic waste nylon-66 into dibenzoyl derivative of hexamethylenediamine (DBHMD) and adipic acid. The degradation of waste nylon-66 was performed at different times and temperatures to understand the efficiency of ionic liquids.

MATERIALS AND METHODOLOGY

Materials

1-Methylimidazole (99% pure) required for the synthesis of ILs was obtained from Sisco research laboratories. 1-Chlorobutane, magnesium sulfate, acetonitrile, dichloromethane, benzoyl chloride, methanol, ethanol etc. were of analytical grade. 5NHCl and 5N NaOH solutions were prepared by using double distilled water.

Synthesis Of [bmim]BF4 and [bmim]PF6 ionic liquid

The Synthesis of ILs was carried out in two steps. The first step involves the formation of quaternary imidazolium ion followed by the anion exchange method as the second step to form the required ionic liquid. For the synthesis of [bmim]BF_4, a mixture of 7.38 g (.09 mol) of 1-methylimidazole and 9.2 g (.1 mol) of 1-chlorobutane, was refluxed at about 70-80°C for 23-24 hours. The reaction mixture was allowed to cool and repeatedly extracted using water to remove unreacted starting material and any by-products. An organic layer 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was obtained as an intermediate. It was dried over magnesium sulfate. For anion exchange, 0.51 g (.03 mol) of [bmim]Cl in acetonitrile and aqueous solution of sodium tetrafluoroborate ($NaBF_4$) (3.27 g,.03 mol) was constantly stirred for several hours at room temperature. After the removal of NaCl, filtrate which mainly contains [bmim]BF_4 was subjected to reduced pressure to remove the acetonitrile and water using a rotary evaporator. The obtained viscous liquid of [bmim]BF_4 was washed with dichloromethane and separated using a rotary evaporator.

Similarly the synthesis of [bmim]PF_6, an intermediate [bmim]Cl was prepared by the reaction of 1-methylimidazole and 1-chlorobutane. For anion exchange, an aqueous solution of [bmim]Cl (1.74 g,. 01mol) and hexafluoro phosphoric acid (HPF_6) (1.45 g, .01mol) was mixed with constant stirring at room temperature for 5-6 hours. The separation of colorless viscous oil signifies the formation of [bmim]PF_6. The crude IL was washed with deionized water to remove unreacted starting material and other present impurities. Since [bmim]PF_6 is hydrophobic and water insoluble, deionized water was an ideal solvent for the washing process without the loss of IL.

Depolymerization of nylon-66

The collected waste nylon-66 which may be contaminated with dust particles, was cleaned with 1 g/L of nonionic detergent at around 70–80°C for 4-5 hours. Furthermore, washed with distilled water and dried in the oven. For depolymerization, 0.2 g of waste nylon-66, 20 mL of 5 N HCl, and 2.2 g (0.1 mol) of [bmim]BF_4 as a catalyst were refluxed in the range of 100-140^{0}C for 5-7 hours. The contents of the reaction mixture were cooled at room temperature. It was neutralized with 5 N NaOH to make a slightly alkaline solution. The addition of benzoyl chloride (C_6H_5COCl) in an alkaline solution, the dibenzoyl derivative of hexamethylene diammine (DBHMD) precipitates out. For the recovery of adipic acid as a monomer, the filtrate was extracted with 20 mL ethyl acetate 10 times. By evaporating ethyl acetate in a vacuum, the colorless crude product adipic acid was obtained. Similarly, the same experiment was performed by using 2.8 g (0.1 mol) of [bmim]PF_6 as a catalyst for the hydrolysis of waste nylon-66. The obtained DBHMD and adipic acid was recrystallized with ethanol and methanol respectively.

RESULT AND DISCUSSION

Characterization of an Ionic Liquids (ILs)

Ionic liquid synthesis, takes place in to two steps, quaternization step which involves the formation of [bmim]Cl as an intermediate followed by an anion exchange method to obtain the desired ionic liquid. The faint yellow viscous IL [bmim]BF_4 and colorless [bmim]PF_6 was obtained as 83.40% and 82.06% respectively. Both the ILs was characterized by ^{1}H NMR technique.

^{1}H-NMR (δ ppm) [bmim]BF_4 (DMSO): 0.89 [t, 3H, (CH_3), CH_3-CH_2-CH_2-CH_2-], 1.12 [m, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-], 1.93 [m, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-], 3.91[s, 3H, (CH_3), CH_3-N], 4.19 [t, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-N], 7.58 [d, 2H, N-CH=CH-N], 7.96 [s, 1H, (CH), N=CH-N] from Fig. 1. The singlet at δ 2.50 ppm was obtained due to DMSO solvent.

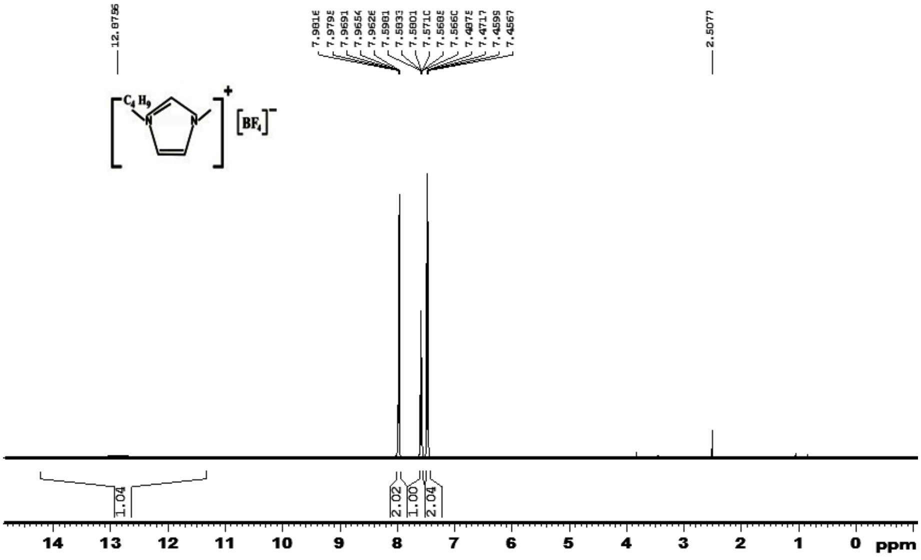

Fig. 1. ^{1}H NMR of [bmim]BF_4

^{1}H-NMR (δ ppm)[bmim]PF_6 (DMSO): 0.93 [t, 3H, (CH_3), CH_3-CH_2-CH_2-CH_2-], 1.33 [m, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-], 1.93 [m, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-], 3.91[s, 3H, (CH_3), CH_3-N], 4.19 [t, 2H, (CH_2), CH_3-CH_2-CH_2-CH_2-N], 7.40 [d, 2H, N-CH=CH-N], 8.44 [s, 1H, (CH), N=CH-N]. The DMSO solvent showed the singlet at δ 2.23 ppm

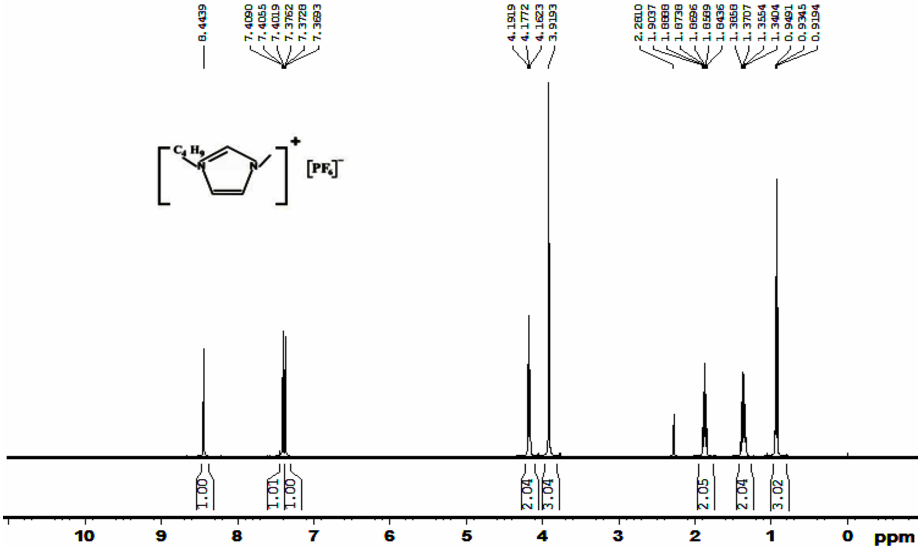

Fig. 2. ^{1}H NMR of [bmim]PF_6

Depolymerization of nylon-66

The hydrolysis of 0.2 g of waste nylon-66 by using 2.3 g (.1mol) of [bmim]BF_4 was performed at different temperatures and time. When we performed the hydrolysis of nylon-66 for seven hours at 120^{0}C in the presence of .1mol of [bmim]BF_4 as catalyst, it yields the maximum amount of DBHMD (2.99 g) and adipic acid (.048 g) and in the absence of catalyst less amount of DBHMD and adipic acid were obtained (Table 1, entry 2 and 5). Further by increasing the temperature to 140^{0}C, the amount of DBHMD and adipic acid decreases. The results are summarized in Table 1.

Table 1: Hydrolysis of waste nylon-66 in IL [bmim]BF_4

Entry	Conc. of [bmim]BF_4 (mol)	Time (hours)	Temperature ^{0}C	DBHMD (g)	Adipic acid (g)
1	0.1	7	100	2.68	.033
2	0.1	7	120	2.99	.048
3	0.1	5	120	2.71	.041
4	0.1	6	120	2.23	.026
5	0	7	120	1.93	.013
6	0.1	7	140	2.87	.032

Due to the moderate water solubility, less viscosity and sufficient mobility of [bmim]BF_4, it initiate the water molecule to interact with the amide groups (-CONH-) present in nylon-66 through hydrogen bonding and electrostatic interactions. This interaction leads to the swelling of nylon-66 and this swelling effect enhances the degradation of nylon-66 into monomers. In comparison to hydrophilic [bmim]BF_4 IL, the hydrophobic [bmim]PF_6 IL has shown the less efficiency to degrade the waste nylon-66 even though the reaction was carried out for nine hours. The results of hydrolysis of nylon-66 in [bmim]PF_6 are summarized in Table 2.

Table 2: Hydrolysis of waste nylon-66 in IL [bmim]PF_6

Entry	Conc. of [bmim]PF_6 (mol)	Time (hours)	Temperature ^{0}C	DBHMD (g)	Adipic acid (g)
1	0.1	9	100	2.01	.020
2	0.1	9	120	2.31	.024
3	0.1	8	120	2.16	.021
4	0.1	7	120	1.55	.016
5	0	9	120	2.06	.011
6	0.1	9	140	2.26	.019

When we performed the hydrolysis of waste nylon-66 at 120⁰C for seven hours in the presence of 2.8 g (.1mol) of [bmim]PF_6 as catalyst, it was observed that it yielded less amount of DBHMD (1.55 g) and adipic acid(.016 g) than in [bmim]BF_4 as a catalyst at same reaction conditions. Even though the reaction time was increased to nine hours, it yields less amount of monomers than [bmim]BF_4. In both experimental works, the maximum amount of monomers was obtained at 120⁰C and further by increasing the temperature to 140⁰C the yield decreased. Due to the water insolubility and less ionic mobility of $[bmim]^+$ and PF_6- ions, it does not help the water molecule to interact with the amide linkages of nylon-66 and resulting less break down of amide linkages. The Hydrophilic IL, [bmim]BF_4, was found to be more effective as a catalyst in the hydrolysis of nylon-66 than hydrophobic [bmim]PF_6 ionic liquid. The water-loving ionic liquid can get deeper into nylon-66 and interacts more strongly with the amide (-CONH-) group, making it easier for the nylon-66 to break down. While due to the high viscosity and less mobility of [bmim]PF_6, it showed less degradation of nylon-66. The monomers BDHMD and adipic acid were characterized by the FT-IR technique.

FT-IR (Adipic acid) cm^{-1}: Adipic acid has shown the broad absorption band in the region of 2500-3000 cm^{-1} due to -OH stretching in the carboxylic group (-COOH). 2909 (-OH stretching in –COOH), 2944-3003 (C-H stretching in >CH_2), 1532 and 1440 are due to C-O and C-C stretching respectively.

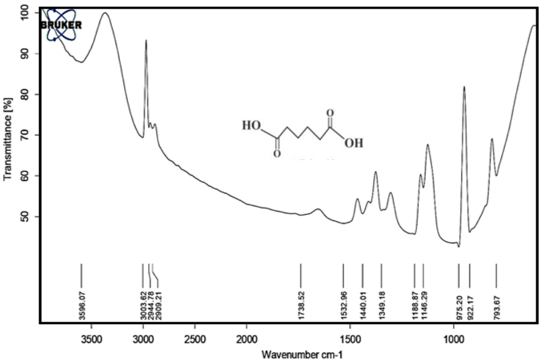

Fig. 3. FT-IR of adipic acid

FT-IR (BDHMD) cm^{-1}: 3510(N-H stretching), 1650 (C=O stretching), 1521, 1450.76, 1319 (C=C stretching in benzoyl group), 1276.14 (C-C stretching in CH_2 groups). The large number of vibrations below the 1500 cm^{-1} (fingerprint region) is due to C-C, C-N stretching and bending vibrations. Due to the symmetrical structure of DBHMD, only one peak for N-H and C=O stretching was obtained.

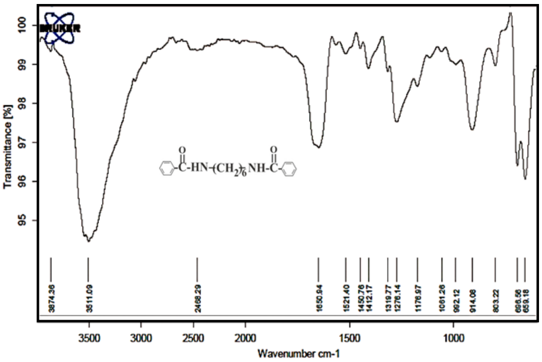

Fig. 4. FT-IR of BDHMD

CONCLUSION

Ionic liquids (ILs), hydrophilic or hydrophobic can degrade nylon-66, however, they do so in diverse ways and to differing degrees of efficiency. Hydrophilic IL [bmim] BF_4 has the ability to connect powerfully with electrostatic interactions with the polar amide groups (-CONH-) found in nylon-66. Because of this interaction, the polymer matrix swells more easily, making it simpler to break down. However hydrophobic IL [bmim]PF_6 has a low affinity for water but found the sufficient potential to disrupt the packing of nylon-66 through the non-polar interaction. It can alter the physical structure nylon-66 and make it susceptible to breakdown. IL [bmim]PF_6 may not interact directly with the amide linkage but is still found to degrade the nylon-66. The use of ILs works as a "greener solvent" because it can be recovered at the end of reaction and reused for 3-4 times without changing its structure and efficiency. The use of ILs provides a potential pathway for degradation of nylon-66 in to their useful chemical components. The degradation of waste nylon by ILs reduces the environmental pollution and this approach aligns with the principle of green chemistry. Future research should on the investigating the new type of ionic liquids and its interactions with the nylon-66 and also the optimization study of degradation of waste nylon-66 at different reaction conditions like concentrations of IL, temperature, reaction time, etc.

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Conflict of interest

The author declares that there is no conflict of interest.

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