Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE AS GREENER SOLVENT FOR DEGRADATION OF NYLON - 6

Sunil Chikte, Swapnil Madhamshettiwar
Sardar Patel Mahavidyalaya, Chandrapur
**Corresponding author: sunilchikte78@gmail.com*

ABSTRACT

This work consist of the degradation of waste plastic by using the ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) as a greener solvent for the recovery of monomer instead of using the commercial hazardous solvents. This method provides the green approach for the recyclable of waste plastics and thus for the clean environment. In this work degradation of nylon-6 (polyamide) performed by distillation method under normal pressure in nitrogen atmosphere at about 280-310 degree Celsius. The degradation took place within five hours. The monomer ϵ-caprolactum obtained by distillation method was in appreciable yield and the recovered ionic liquids can be used for four to five times without changing its efficiency. Addition of catalytic amount of DMAP (N, N-dimethylaminopyridine) promoted the degradation of nylon-6 effectively. In this work the degradation of nylon-6 were carried out at different temperature and at different catalyst concentration. The maximum yield of ϵ-caprolactum was obtained at 10 wt% of DMAP and at 300 degree Celsius, and the recovery of ionic liquid was also maximum.

Keywords: Ionic liquid, Degradation, Polyamide, Chemical recycling, Catalyst.

1. INTRODUCTION

Degradation (depolymerization) is the urge of today's world as the waste plastics becoming a great challenging to the green environment. For the degradation of waste plastics, the ionic liquids (IL_S) can be used in a very simple way instead of commercial solvents like HCl, H_2SO_4 etc. Ionic liquids are the combination of cations and anions which are the liquid at low temperature and at around room temperature. Due to the very unique properties of ionic liquids like non-volatility, thermal and chemical stability and non-flammability [1-4] makes it different from the commercial solvent. Ionic liquids are also known as tunable or designable solvents as their physical and chemical properties changes with the type of cation and anion. The ionic liquids consist of cations like N-alkylpyridinium, N,N-dialkylimidazolium, alkylimidazolium, alkylphosphonium and alkylammonium etc. and organic and inorganic anions such as BF_4^-, Cl^-, I^-, $AlCl_4^-$, PF_6^-, NO_3^-, CH_3COO^-, $CF_3SO_3^-$ in which the cations are weakly coordinated with the inorganic or organic anions. The combination of different cations and anions gives around theoretically 10^{18} variety of ionic liquids. Due to the low vapor pressure of ionic liquids, it has more potential and replaces the volatile solvents in large number of chemical reactions. Now a day's ILs has widely being used as solvent reactant and catalyst in synthesis process. It has been also used as the absorption media in the gas separation and also it has wide applications in electrochemistry like batteries, solar cell etc. [5-8]. Now a day's ILs has widely being used as solvent reactant and catalyst in synthesis process [9].

In today's world where the use of plastics is tremendously increasing in daily routine life, so development of an effective method for the recycling of waste plastics is one of the major environmental issue. To overcome this problem, among the different techniques, the chemical degradation of waste plastic into their monomer supports the sustainable development of current society [10]. Degradation or depolymerization is one of the methods to convert the waste plastic into its monomer which can be again reused to form usable plastic. For the efficient progress of degradation, input of energy is required (endothermic reaction). A different chemical method has been employed for the degradation of waste plastic into its monomeric material. Supercritical and subcritical fluids [11-12], pyrolysis [13-14] and acid hydrolysis [15-16] are the simple ways to degrade the waste plastic but the reaction conditions are very hard.

Though these are the advantageous methods for the depolymerization but due to high temperature and pressure conditions make it difficult to handle, therefore special glass apparatus and precautions are required to prevent the fire. Under these circumstances ionic liquids are the new emerging liquids as greener solvents for the depolymerization of waste plastics. Due to the unique physic-chemical properties of ILs like non-volatility, low vapor pressure, chemical and thermal stability over a wide range of temperature, it can be used in simple glassware without any risk of fire. The main advantage of ionic liquids that it can be repeatedly used for four to five times with its same efficiency. Many researchers worked on the use of ionic liquids in depolymerization process. Ionic liquid 1-butyl-3 methylimidazoliumchloride ([bmim]Cl) dissolves cellulose 10 wt % by heating [17]. Similarly Zhang H. et al. worked on the effective producing regenerated cellulose by using novel ionic liquid 1-allyl-3-methylimidazolium chloride ([amim]Cl) [18]. Chloroaluminate (III) ionic liqiuid was used for the catalytic cracking of polyethylene to light alkanes [19]. Kamimura et al worked on the degradation of polyamide (nylon-6) into its monomer є-caprolactum by using the ionic liquid based on the quaternary ammonium ion as cation [20].

In this research paper we worked on the determination of molecular weight of nylon-6 by viscosity method and degradation of nylon-6 into its monomer є-caprolactum. For degradation we used the 1-ethyl-3-methylimidazolium tetrafluoroborate water soluble ionic liquid. Due to its water miscibility, it provides the high ionicity and reactivity for the degradation process [21-22].

2. EXPERIMENTAL

2.1. Determination of molecular weight of nylon- 6

The intrinsic viscosity of nylon -6 (polyamide) solutions in m-cresol is used to determine the average molecular weight by using the Mark- Houwink empirical equation as mentioned below.

$$[\eta] = KM^{\alpha}$$

Where $[\eta]$ is the intrinsic viscosity, K and α are the constants depending up on the solvent and M is the average molecular weight of the polymer. The intrinsic viscosity of the nylon-6 solution can be determined experimentally by measuring the specific viscosity by equation:

$$\eta_{sp} = \eta_r - 1$$

Where η_{sp} is the specific viscosity and η_r is the relative viscosity.

The relative viscosity is the ratio of the flow time of the solution to the flow time of pure solvent.

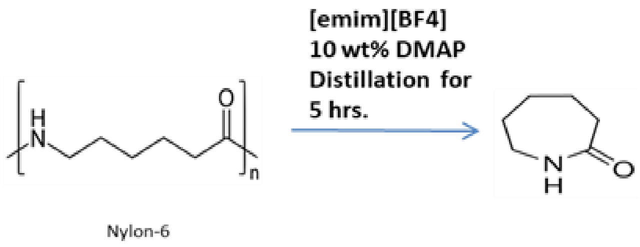
Relative viscosity = flow time of solution /Flow time of solvent.

The intrinsic viscosity is given as the limit of the ratio of the specific viscosity (η_{sp}) and the polymer solution concentration i.e. reduced viscosity (η_r) approaches to zero as given by:

$$[\eta] = \lim_{c \to 0} \eta_{sp} / c$$

2.2. Degradation of nylon-6 in 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4]

0.2 gram of nylon-6 having average molecular 22,000 was added in 2.3 gram of [emim][BF_4] in the presence of 0.02 gram (10 wt%) of N, N,-Dimethylaminopyridine (DMAP) as catalyst. The mixture was allowed to distill under normal pressure at 300°C for near about five hours in nitrogen atmosphere with constant stirring. In this work distillation process was used to obtain the monomer i.e. є - caprolactum. The distillation method found to be more convenient than the laborious extraction method. The extraction method involves the extraction of the reaction mixture with diethyl ether solvent (10 ml × 25 times). The concentration of ether phase gives the crude product of є -caprolactum.



Scheme 1: Degradation reactions of nylon-6

3. RESULTS AND DISCUSSION

3.1. Determination of molecular weight of nylon-6

The measurement of viscosity of nylon-6 solution in m-cresol solvent by using Ostwald's viscometer gives the average molecular weight. The viscosity method gives the weight average molecular weight and specific viscosity (η_{sp}) is assumed to be the simple linear function of polymer concentration (c). Experimentally, the different concentrations of nylon-6 were prepared in the m-cresol solvent and the specific viscosities were measured for each solution (table 1).

The plot of reduced viscosity (η_{sp}/c) and inherent viscosity ($\ln \eta_r/c$) verses concentrations were extrapolated to zero concentration gives the high precision intrinsic viscosity [η]. The value of intrinsic viscosity is nearly same for the plot of reduced viscosity and inherent viscosity verses concentration (Fig.1). Mark-Houwink equation provides the simple procedure to determine the weight average molecular weight of polymer.

$$[\eta] = KM^{\alpha}$$

The value of intrinsic viscosity [η] from fig.1 is 1.05. The constant K and α for m-cresol solvents are 2.41×10^{-3} and 0.61respectivly. The average molecular weight for nylon-6 was found to be 22000 approximately.

Table 1: Experimental flow time, reduced viscosity, specific viscosity

Conc. of nylon-6 (g/25 ml)	Flow time (seconds)	Relative viscosity (η_r)	Specific viscosity ($\eta sp = \eta_r$-1)	Reduced viscosity ($\eta sp/c$)	ln η_r	Inherent Vis. (η_{inh}) ($\ln \eta_r /c$)
0.075	351	1.382	1.02	5.093	0.3235	4.313
0.0625	324	1.275	0.275	4.40	0.2429	3.886
0.05	301	1.185	0.185	3.70	0.1697	3.394
0.0375	284	1.116	0.116	3.10	0.1097	2.925
0.025	269	1.058	0.058	2.30	0.0563	2.252
0.0125	259	1.02	0.022	1.75	0.0198	1.584
m-cresol	254	--	--	--	--	--

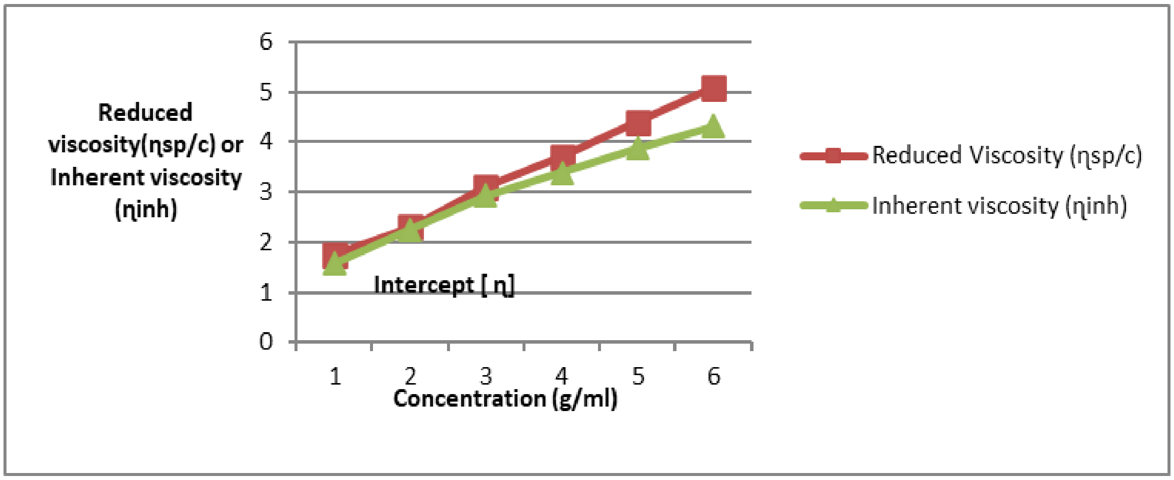


Fig. 1: The plot of reduced viscosity and inherent viscosity verses concentration

3.2. Degradation of nylon-6 in [emim][BF$_4$] as ionic liquid

Ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (extra pure 97%) with CAS no.143314-16-3 were purchased from Sisco Research Laboratory Pvt. Ltd. Mumbai and used without any further purification. The 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF$_4$]) ionic liquid which is water soluble, having low vapor pressure and chemically and thermally stable at high temperature was used for the degradation of the nylon-6 into its monomer ϵ-caprolactum. In this work we performed the degradation of nylon-6 to convert in to ϵ-caprolactum under different conditions and examined results which are summarized in table 2.

Degradation of nylon-6 was performed by distillation method at different temperatures and in absence and presence of N, N-dimethylaminopyridine (DMAP) for five hours in nitrogen atmosphere. Very less degradation took place at 280°C in the absence of DMAP catalyst and the recovery of [emim][BF$_4$] was maximum (sr.no. 1). Then we added the 0.02 gram of DMAP catalyst (10 wt%) and performed the depolymerization at 300, 310 and 320°C. It was found that the addition of DMAP catalyst enhance the efficiency of degradation of nylon-6 into its monomer. The yield of ϵ-caprolactum was maximum (55%) at 300°C and recovery of ionic liquid was also sufficient (sr. no. 2). The product ϵ-caprolactum was characterized and confirmed by FT-IR (fig.2) which shows the peaks near about 3300 cm^{-1} and 1700 cm^{-1} due to N-H and C=O stretching respectively. After the complete removal of ϵ-caprolactum monomer from the reaction mixture by distillation process, the remaining ionic liquid can be reused without changing its efficiency. The recovered [emim][BF_4] ionic liquid after degradation of nylon-6 was characterized by FT-IR (fig.3). This spectra was compared with the pure [emim][BF_4] (fig.4) and the both spectra were found similar.

Table 2: Degradation of nylon-6 in different conditions

Sr. no.	DMAP (wt %)	Time(min.)	Temp. (°C)	Є-Caprolactum (% yield)	Recovery Of IL (%)
1	0	300	280	10	94
2	10	300	300	55	84
3	10	300	310	38	85
4	10	300	320	32	81

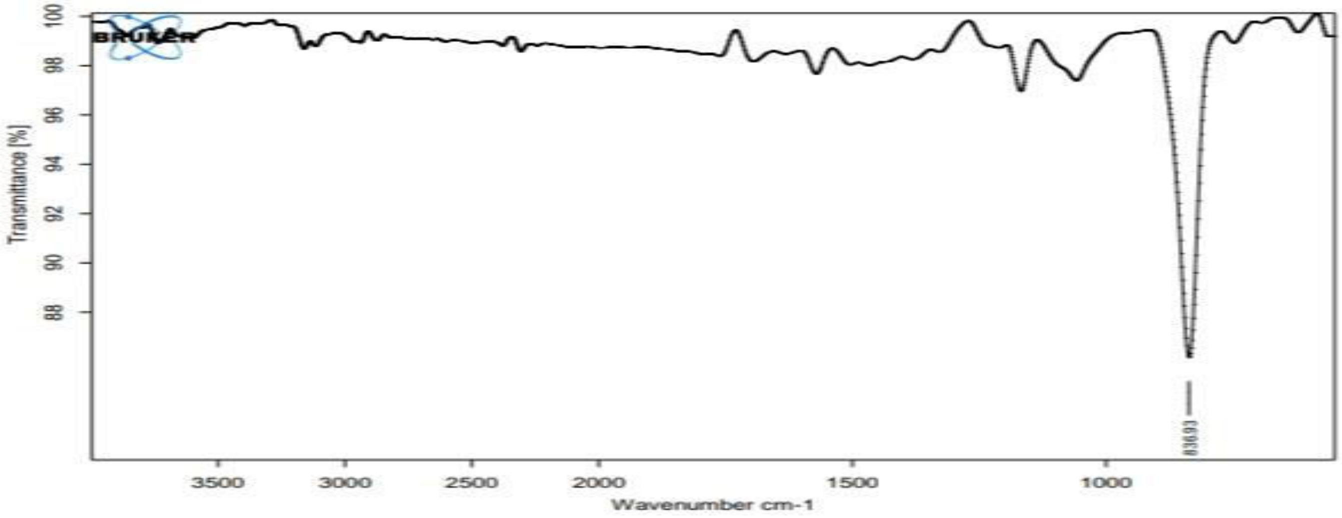


Fig. 2: FT-IR of ϵ- caprolactum

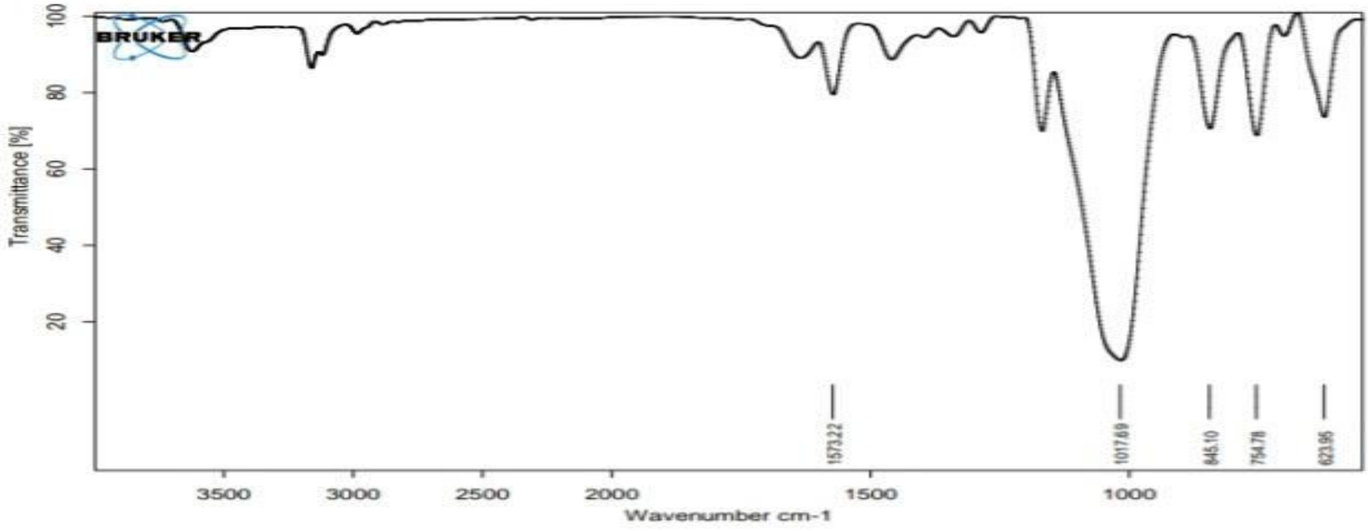


Fig. 3: FT-IR of recovered [emim][BF4]

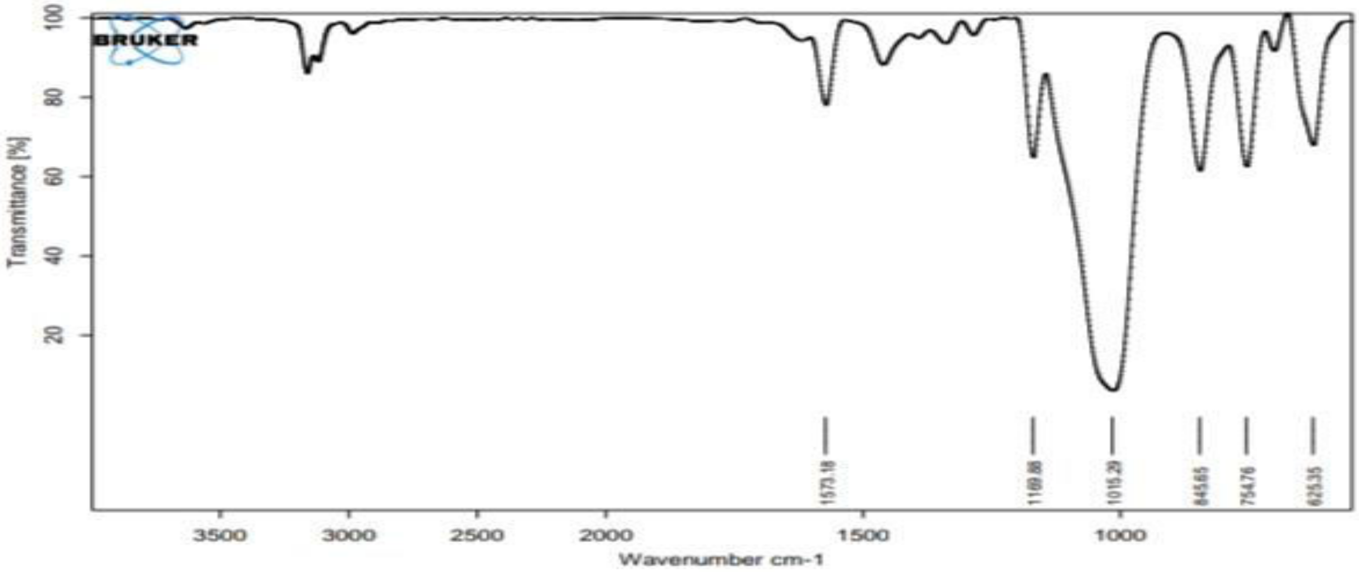


Fig. 4: FT-IR of pure [emim][BF4]

4. CONCLUSION

The experimental method for the degradation of nylon-6 (polyamide) in to its monomer є-caprolactum was performed in a very simple way. The reaction was carried out at normal pressure without any requirement of special apparatus. The monomer, є-caprolactum was directly obtained from the reaction pot by distillation method which is very easier than the laborious isolation method by ether solvent and also reduces the use of chemicals. The ionic liquid [emim][BF_4] which was recovered from reaction pot can be used for four to five times without changing its efficiency. In this way the waste plastic can be converted in to its monomer which can be again used for the useful products. The present work provides the simple way for the recycle of waste plastic into its starting material which can again used for useful products. The main feature of this work is the use of ionic liquid as green solvent instead of the commercial solvents.

5. ACKNOWLEDGEMENT

The authors gratefully thanks to Sardar Patel College, Chandrapur (M.S.) for providing the facilities to carried out the experiments. Authors are also thankful to Department of Chemistry, R. T. M. Nagpur University, Nagpur for FT-IR analysis of the samples.

Conflict of interest

While publishing this research paper, the authors have no conflict of interest.

6. REFERENCES

1. Dupont J, Desouza RF, Saurez P, *Chemical Rev*, 2002; **102:**3667.
2. Kosmulski M, Gustafsson J, Rosenholm JB, *Thermochim. Acta*, 2004; **47:**412.
3. Moto H, Yanagida M, Tanimoto K, Nomura M, Kitagawa Y, Y. Miyazaki Y, *Chem. Lett*, 2000; **29:**922.
4. Kaczmarek H, Kamińska A, Świątek M, Rabek JF, Photo-oxidative degradation of some water-soluble polymers in the presence of accelerating agents. *Angew. Makromol. Chemie,*1998; **261-262:**109-121 .
5. Brennecke JF, Maginn EJ, Ionic Liquids: Innovative Fluids For Chemical Processing. *AI Che J*, 2001; **47:**2384-2389.
6. Wasserscheid P, Keim W, Ionic Liquids : New Solutions For Transition Metal Catalysis, Angwew.*Chem. Int. Edit,* 2000; **39:**3773-3789.
7. Welton T, Room Temperature Ionic Liquids, Solvents For Synthesis and Catalysis, *Chem. Rev.*1999; **99:**2071-2083.
8. Wilkes JS. *J. Mol. Catal. Chem*, 2004; **214:**11-17.
9. Weyershausen B, Lehmann K, *Green Chem,* 2005; **7:**9-15
10. Research Association Of Feedstock Recycling Of Plastics (Ed), Technology For Feedstock Recycling Of Plastic Waste, *CMC Books, Tokyo*, 2005.
11. Goto M, *Supercrit J. Fluids*, 2009; **47:**500-507.
12. Goto M, Sasaki M, Hirose T, *J. Mater. Sci.* 2006; **41:**1509-1515.
13. Bockhorn H, Donner S, Gernsbeck M, Hornung A,

Hornung U, *J. Anal . Appl.Pyrol*, 2001; **58:**79-94.

14. Herrera M, Matuschek G, Kettrup A,*Chemosphere*, 2001; **42:**601-607.
15. Shukla S, Harad AM, Mahoto D, *J. Appl. Polym. Sci,* 2006; **100:**186-190.
16. Klun U, Krzan A, *Polym. Adv. Technol*, 2002, **13:**817-822.
17. Swatloski RP, Spear SK, Holbrey JD, Rogers RD, *J. Am. Chem. Soc* ,2002; **124:**4974-4981.
18. Zhang H, Wu J, Zhang J, He JS, *Macromolecules*, 2005; **38**:8272.
19. Adams CJ, Earle MJ, Seddon KR, *Green Chem*, 2000; **2:**21.
20. Kamimura A, Yamamoto S, *Org. Lett*, 2007; **9:**2533.
21. Kamimura A, Okagawa T, Oyama N, Otsuka T, Yoshimoto M, *Green Chem*, 2012; **14:**4962-4967.
22. MacFarlane DR, Forsyth M, Izgorodina EI, Abbott AP, Annat G, Fraser K, *Phys.Chem*, 2009; **11:**4962-4967.