Determination of Impurities in Industrial Caprolactam Produced from Toluene by SPME and GC–MS

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ABSTRACT: Solid-phase microextraction (SPME) in combination with gas chromatography-mass spectrometry (GC–MS) was applied to study the impurities in industrial caprolactam produced from toluene. Various nitriles, lactones, amides, and alcohols were detected to be the main impurities in caprolactam products. Trace amounts of heterocyclic compounds, which had great effects on the quality of caprolactam, were also successfully detected. Those were pyrrole, 2-ethyl-3-methyl pyrazine, 5,6,7,8-tetrahydroquinoxaline, quinoxaline, 2,3-dimethyl quinoxaline, 2-pyridinamide, etc. The effects of some impurities on caprolactam quality and the polymerization of caprolactam as well as the possible origin of the main impurities were also discussed. This could be of great importance to the industrial purity control of caprolactam. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 000: 3141–3144, 2006

Key words: impurities; caprolactam; monomers; chromatography; mass spectrometry; SPME

INTRODUCTION

Caprolactam is one of the most important raw materials for the versatile polyamide-6 production with a wide application in the artificial fiber industry as well as a structural material in the motorization and electronics industry. In the recent years, there has been an ever increasing demand for caprolactam as the flourish of communication, electronic, automobile and costume industries brings the rise of demands for nylon and synthetic fiber. The world demands for caprolactam in 2004 reached to about 4000,000 tons and it was estimated by TecnonOrbiChem Company that the production of it would be 4980,000 tons in 2010 and that the demands would arrive at 5000,000 tons in 2015.[1,2]

The main industrial synthesis processes now existing all over the world are divided into four categories.[3,4] First, the most common one, is through Beckmann rearrangement of cyclohexanone oxime, which is formed by the reaction of cyclohexanone and hydroxylamine. The second one is the direct formation of cyclohexanone oxime from cyclohexane without the formation of cyclohexanone and without the use of hydroxylamine. However only few companies have still employed this method for the production of caprolactam because some difficulties existing in the course of its industrialization still have not been satisfactorily resolved. The third one is by the ammonolysis of caprolactone, which is obtained by the reaction of cyclohexanone and peracetic acid. The last one is based on the oxidation of the toluene, in which the toluene is first oxidized into benzoic acid and then the benzoic acid was hydrogenated into cyclohexanecarboxylic acid, which could be successionally reacted with nitrosylsulfuric acid to form caprolactam. It was developed by the SINA company in early sixties and was broadly applied in 1970s and 1980s. But some companies stopped the production afterward because of its relatively high cost or the matter of raw materials. Up to the present, Shijiazhuang Chemical and Chemical Fiber company (the subsidiary of China Petroleum and Chemical Corp.) is the only company in the world employing this process for the production of caprolactam. Nevertheless, caprolactam production in Shijiazhuang fills up the ever increasing demands for caprolactam in Asia, especially in China. Recently, a new method for the production of caprolactam from K/A-oil (a mixture of cyclohexanone and cyclohexanol) using *N*-hydroxyphthalimide (NHPI) as the catalyst was investigated by the researchers of Kansai University in Japan.[5] This route provides a more economical and environmental friendly (salt free) process than those by the current methods. Therefore, it is considered to be a promising technology, though it is still in the course of its industrialization.

It is well known that certain impurities in caprolactam directly influence the quality of caprolactam products and thereby affect the properties of the synthetic fibers. Therefore, it is the critical issue to determine the impurities in caprolactam and thereby to

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understand their influence on the products. Lots of analytical work has been done on the impurities of caprolactam, such as Raman spectroscopy,[6] gas chromatography (GC),[4,7–9] high performance liquid chromatography (HPLC)[10] and gas chromatography–mass spectrometry (GC–MS),[11] etc. However almost all of work was focused on analyzing impurities in caprolactam produced from cyclohexanone. Few reports on the impurities in caprolactam produced from toluene is available except a few literature in 1980s and there were numerous unknown compounds that were unable to be identified depending on the analytical instruments of that time.[3,12] Moreover, it is known that the impurities presented in caprolactam depend upon the manufacturing process.[3] Different industrial process brings different impurities. Thus, the aim of our work was to determine the impurities in caprolactam produced from toluene. Their potential effects on the product quality and their possible origin in industry were also discussed. Solid-Phase Microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) had come to our preferable choice because this method integrated the advantages of SPME, such as high sensitivity, simplicity, low cost, compatibility with analytical systems, automation, and the solvent-free extraction,[13] with the high separation ability and resolving power of GC–MS. Another important reason for us to use the SPME and GC–MS for the analysis was that the possible interference of caprolactam matrix could be reduced or avoided, therefore, low level impurities could be detected. All this advantages enable the application of SPME and GC–MS to the industrial purity control of caprolactam.

EXPERIMENTAL

Materials

The crude caprolactam was provided by Shijiazhuang Chemical and Chemical Fiber company, China. All standards were purchased from Aldrich (Shanghai, China). The SPME holder for manual sampling and the fiber coated with a 65 μm Carbowax-divinylbenzene was purchased from Supelco (Bellefonte).

Sample preparation and headspace SPME procedures

The crude caprolactam was distilled in the industrial continuous distillation unit and the first fraction, 98% of which was caprolactam, was used for the analysis. 1.0 g of the sample was added into a 20 mL glass vial with a Teflon-coated septum. After equilibrium for 30 min at 25°C, the SPME fiber was exposed to the headspace above the glass vial for 30 min. After completion of the SPME step, the analytes absorbed in the SPME fiber were analyzed by GC–MS

GC–MS analysis

The GC–MS analysis was carried out on a HP6890 Gas Chromatograph with a HP5973 mass spectrometric detector. Analytes were thermally desorbed from the coated fiber of the SPME in the hot injector of the GC (the fiber remained for 3 min in the injector) and were separated on a HP INNOWAX capillary column, 30 m $\times$ 0.25 mm ID and 0.25 μm phase thickness. The GC column was maintained at 40°C for 6 min, ramped at a rate of 5°C/min to 220°C and held at this temperature for 2 min. The split–splitless injector was used, and the injector was operating in the splitless mode. Temperatures of the injector and the transfer line were 250 and 280°C, respectively. The carrier gas used was helium, which was set at a constant flow-rate of 1 mL/min. The mass spectrometer was operated in electron impact mode (EI, 70 eV) and the masses were scanned over an *m/z* range of 35–300 amu.

RESULTS AND DISCUSSION

SPME and GC–MS analysis of impurities in caprolactam

Because of the great variety and low concentration of impurities in caprolactam, the existence of large amount of caprolactam matrix usually interferes the determination of these impurities.[9] SPME could, to some extent, overcome this shortcoming because of its particular characteristics. In the present work, the SPME fiber was exposed to the headspace above the glass vial so that the fiber was enriched with most of the volatile impurities but few caprolactam. Caprolactam was observed for only 4% of the total chromatographic peak areas after SPME procedure (Table I), while the initial concentration of caprolactam was 98%.

In the present work, 46 compounds in the first fraction were identified (shown in Table I). The GC–MS chromatogram of the sample was shown in Figure 1. And the peak identification was based on the Nist02 mass spectral library. The heterocyclic compounds, which were suggested to have great effects on the caprolactam quality, were further confirmed by direct comparison with authentic samples on the basis of the retention time and mass spectrometry. However, peak 13 and 29 (shown in Fig. 1) could not be identified for certain by a comparison of the mass spectra published. It was observed that the impurities composed of relatively large amount of nitriles and lactones, such as cyclohexanecarbonitrile, benzonitrile, 3-methyl cyclohexenecarbonitrile, 5-ethyldihydro-2(3H)-furanone, *cis*-hexahydrophthalide, and dihydro-5-methyl-2(3H)-furanone. Some ketones, oximes, alcohols and amides were detected too, such as cyclohexanone oxime, cyclohexanemethanol, acetamide and propanamide, etc. Meanwhile, various heterocyclic

TABLE I
Impurities in the Former Distillate of Crude Caprolactam (Including Caprolactam)

No	Component	Relative content (%)	Identification
1	Cyclohexanone	1.22	MS
2	2-methyl-2-cyclopenten-1-one	0.37	MS
3	1-cyclohexyl-ethanone	0.60	MS
4	cyclohexanol	0.28	MS
5	1,2,4,5-tetramethyl-benzene	0.02	MS
6	3-methyl-2-cyclohexen-1-one	0.01	MS, Std
7	1-cyclohexyl-1-propanone	0.08	MS
8	Cyclohexanecarbonitrile	34.81	MS
9	3-methyl-2-cyclopenten-1-one	0.10	MS
10	Pyrrole	0.05	MS
11	3-methyl cyclohexenecarbonitrile	8.82	MS
12	Cyclohexanemethanol	6.54	MS
13	Unknown	0.30	
14	2-methyl-1H-pyrrole	0.22	MS
15	Dihydro-3-methyl-2(3H)-furanone	1.42	MS
16	Benzonitrile	14.13	MS
17	Dihydro-5-methyl-2(3H)-furanone	2.58	MS
18	Tetrahydro-2H-pyran-2-one	0.79	MS
19	Butyrolactone	0.49	MS
20	2-ethyl-3-methyl pyrazine	0.04	MS
21	*N*-ethyl-propanamide	0.12	MS
22	4-methyl-benzonitrile	0.11	MS
23	5-ethyldihydro-2(3H)-furanone	11.48	MS
24	4-methyl-benzonitrile	0.28	MS
25	5,6,7,8-tetrahydroquinoxaline	0.56	MS, Std
26	3-methyl-5,6,7,8-tetrahydroquinoline	0.18	MS
27	Aniline	0.07	MS, Std
28	Acetamide	1.17	MS
29	Unknown	0.29	
30	2-methyl-5,6,7,8-tetrahydroquinoxaline	0.12	MS, Std
31	Cyclohexanone, oxime	1.18	MS, Std
32	Propanamide	1.18	MS
33	*N*-butyl acetamide	0.13	MS
34	1-phenyl-cyclohexene	0.04	MS
35	Benzyl alcohol	0.07	MS, Std
36	Butanamide	0.13	MS
37	Quinoxaline	0.34	MS, Std
38	2-pyridinamide	0.04	MS, Std
39	1,2-cyclohexanediol	0.12	MS
40	2-methyl quinoxaline	0.07	MS
41	1-(1H-pyrrol-2-yl)-ethanone	0.01	MS
42	2-cyclohexen-1-one, oxime	0.05	MS
43	*Cis*-hexahydrophthalide	4.18	MS
44	2,3-dimethyl quinoxaline	0.03	MS, Std
45	2-piperidinone	0.08	MS
46	Hexahydro-3-methyl-2H-azepin-2-one	1.00	MS
47	Caprolactam	3.95	MS
48	1,2,3,4,5,6,7,8-octahydro acridine	0.15	MS

MS: mass spectrometry; Std: direct comparison with authentic samples (standards) on the basis of the retention time and mass spectrometry.

compounds, though in very low content, were successfully detected in our sample. Those were pyrrole, 2-ethyl-3-methyl pyrazine, 5,6,7,8-tetrahydroquinoxaline, quinoxaline, 2,3-dimethyl quinoxaline, 2-pyridinamide and so on.

Effects of impurities on caprolactam quality and the polymerization of caprolactam

The effects of impurities on the quality of caprolactam and the properties of caprolactam polymer have already been investigated.[14–17] Because of the strong absorbency around 290 nm, trace amounts of heterocyclic compounds detected in the sample were likely to greatly influence the ultra-violet absorption (UV) of caprolactam at 290 nm, which is one of the most important quality indexes of caprolactam products. Therefore, the detection of them could be significant to the industrial quality control of caprolactam products as well as the optimization of the conditions of caprolactam production. Moreover, the existence of various

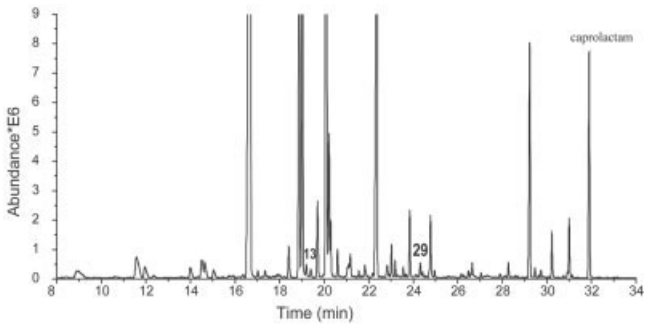

Figure 1 The GC–MS chromatogram of the sample.

oximes could have adverse effect on the color (CO) of caprolactam. And it is known that high values in the ultra-violet absorption and color units generally involve a colored polymer.[15] In addition, relatively high amounts of amides and alcohols, such as acetamide, propanamide, cyclohexanol, etc., were undesirable because their functional groups or their oxidation derivatives (for instance, oxidation of cyclohexanol will generate hexanedioic acid) could react with the end groups of the polymer intermediates and consequently influence the chain propagation. This could yield polymers with relatively low molecular weight during the polymerization of caprolactam.[16,17] Moreover, the viscosity of the polyamide could also be affected by the cyclohexanone, cyclohexanone oxime, or aniline existed in caprolactam because they could react with the amidic or carboxylic groups of the polymer.[17]

Possible origin of the main impurities in caprolactam

It was reported that the impurities could originate from raw materials, intermediate or by-products formed during reactions and the processes of storage and transportation.[4] In the present work, the caprolactam was produced from toluene and this process included three basic reactions: oxidation of toluene into benzoic acid; hydrogenation of benzoic acid into cyclohexanecarboxylic acid; and finally the reaction of cyclohexanecarboxylic acid with nitrosylsulfuric acid for the formation of caprolactam. The main impurities in the sample might come from the second and the third step reaction. Nitriles such as cyclohexanecarbonitrile, benzonitrile, and 3-methyl cyclohexenecarbonitrile (the major components in impurities) were likely to be obtained from the second step reaction because of the incomplete hydrogenation of benzoic acid. Various lactones such as 5-ethyldihydro-2(3H)-furanone were possibly generated in the third step reaction. In addition, 3-methyl cyclohexenecarbonitrile, hexahydro-3-methyl-2H-azepin-2-one, and the relative derivates were probably related to the existence of dimethylbenzene in the raw material.

CONCLUSIONS

The impurities in caprolactam produced from toluene were identified by SPME and GC–MS. Forty-six compounds, which include nitriles, lactones, amides, alcohols and trace amounts of heterocyclics, etc., were successfully detected. This would be significant to understand the formation of the impurities in caprolactam and their potential effects on caprolactam products. The SPME and GC–MS procedure described offers some advantages in detecting various impurities (including trace level impurities) in caprolactam, which could enable it to be a potential and valuable tool to detect impurities in caprolactam as well as for the rapid industrial quality assessment of caprolactam.

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