

Analysis of Minor Additives and Polymer in Used-stripper Using Pyrolysis-Gas Chromatography/Mass Spectrometry and Electrospray Mass Spectrometry

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The trace polymer and additives in used stripper solutions were analyzed by a combination of Py-GC/MS and ESI-MS. In the comparison of the pyrolysates produced by the pyrolysis of the pure stripper and photoresist at 500 °C, the presence of novolac polymer in the used stripper was confirmed by the presence of the characteristic peaks of its pyrolysates, such as those of the methylphenol, di-methylphenol and methylenebis(methylphenol) isomers. The intact trace polymer was measured by ESI-MS, which showed the distribution of oligomers at intervals of 120 Da, indicating di-methylphenol to be the repeat unit. Additional MS/MS measurements demonstrated that the end group is methylphenol and the repeat groups are di-methylphenol. Some modified oligomers caused by the methylation or di-methylation of the repeat unit were also identified. Although the polymer is only present at a trace level in the used stripper, these combined analytical methods provided the means to qualify the stripper solution through the identification and structural determination of the polymer.

Key Words: Novolac, Stripper, Photoresist, Pyrolysis, Electrospray ionization

Introduction

In the thin film transistor liquid crystal display (TFT-LCD) manufacturing processes, the photoresist (PR) used to form a patterned coating on the surface is removed after the exposure, developing and etching steps using a liquid called a stripper.¹ The repeated stripping processes of the substrates affects the PR and causes impurities to be piled up in the stripper solution. These accumulated components obstruct the removal performance of the stripper, which risks to impair the creation of delicate patterns over the entire surface due to losing its function. Accordingly, analytical techniques of the minor impurities in the used stripper are needed to determine the limit of the stripping ability.

Stripper solution is an organic solvent mixture with some additives, which chemically alter the PR so that it does not adhere to the substrate.² This volatile solution can be easily separated and determined by GC/MS, while the determination of the PR detached from the substrates during the stripping process is based on a mixture of polymer resin and photo active compounds (PACs) whose high molecular weight and non-volatile property require other analytical approaches. The chemical structures of these substances have been investigated using techniques such as X-ray-photoelectron spectroscopy (XPS),³ time of flight secondary ion mass spectrometry (TOF-SIMS),^{4,5} nuclear magnetic resonance (NMR),⁶ and infrared spectroscopy (IR),⁷ although the analysis results were obtained from the surface of the substrates not from the stripper solution itself.

Pyrolysis has been used for a long time in qualitative and quantitative composition analysis, as well as for the structure exploration of synthetic polymers.⁸⁻¹³ Recent developments have focused on the enhanced detection of low level chemical species in polymers. The detection of low content additives, including fillers, pigments, antioxidants, stabilizers, flame

retardants, plasticizers, lubricants and other modifiers in the polymer, was simplified by using a combination of multiple temperature step and selected ion chromatography.¹⁴⁻¹⁶ These methods take advantage of thermal desorption to separate the low molecular weight additives before the polymer chain undergoes decomposition.¹⁷⁻¹⁹ Wang studied the analysis of the additives in several types of polymer, in order to demonstrate the utility of pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) as a tool for the characterization of such polymeric materials.²⁰⁻²³ Although the volatile and semi-volatile additives could be thermally removed from the polymer, large molecular weight additives, such as antioxidants and light stabilizers are pyrolyzed along with the polymer matrix and the peaks generated from these additives may be obscured by those from the polymer itself. In order to discriminate the very small peaks of the additives from the major peaks of the polymer matrix, the analysis of pure additive standards added to the polymer may assist in identifying those peaks in the pyrogram which differ from those of the products resulting from the pyrolysis of the polymer matrix.¹⁴ However, the pyrolysis is not compatible with quantitative determination because an internal standard would be thermally decomposed at the temperature. In just a few papers, the quantitative analysis of additives thermally desorbed at a low temperature was studied to prevent decomposition.^{19,24}

These techniques employing Py-GC/MS were only for the purpose of identifying the minor additives originating from the polymer, so that an appropriate analytical method still needs to be developed for the trace analysis of the polymer removed in the used stripper solution. In this study, a method of determining the trace PR, especially polymer, is established through a combination of pre-drying to remove the volatile stripper constituents and pyrolysis at sequential temperatures. The structural determination of the polymer by electrospray-mass spectrometry (ESI-MS) is also discussed to clarify the characterization of the repeat units and end groups.

Experimental

Chemicals and reagents. All solvents used in this study were obtained from J. T. Baker (Phillipsburg, NJ, USA). Formic Acid (Aldrich, Milwaukee, WI, USA) was used to enhance the ionization efficiencies during the ESI-MS analysis. The photoresist (PR), new stripper and the stripper used in the TFT-LCD manufacturing process were obtained from Dae Won F&C Inc.

Pyrolysis. The pyrolysis of the samples was performed on a Frontier Lab PY-2020iD pyrolyzer (Koriyama, Fukushima, Japan). A 2 μ L aliquot of each sample solution was placed in a platinum sample cup and then dried in an oven at 100 °C for 2 h in order to remove the large quantity of volatile organic solvent. The dried sample cup was inserted into the pyrolyzer chamber that was purged with helium before the pyrolysis. After pre-heating the furnace in the pyrolyzer at 300 °C, the sample was first placed in the middle of the furnace for 1 min and then moved to the top of the furnace where the temperature was maintained at about 50 °C. The pyrolysates produced at this temperature were separated and analyzed by a GC/MS spectrometer coupled directly with the pyrolyzer. The GC/MS conditions are described below. For sequential pyrolysis, the sample was re-located in the middle of the furnace at 500 °C for 1 min and another pyrogram was obtained by GC/MS. Continuing pyrolysis was also performed at 700 °C through the same procedure.

GC/MS. An Agilent GC/MS system composed of an Agilent 6890 gas chromatograph and an Agilent 5975i mass spectrometer (Palo Alto, CA, USA), was used to separate and obtain the mass spectra of the compounds in each sample. The samples were injected in split mode (50:1 ratio). The carrier gas was helium (99.999%) with a flow rate of 1 mL/min and an average velocity of 37 cm/sec. The oven was initially held at 100 °C for 5 min, increased to 300 °C at 10 °C/min, and then held at this temperature for 15 min. A DB-5MS cross-linked 5% phenyl methylsilicone fused-silica capillary column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness) was used to separate the samples. The column was interfaced directly to the electron impact (EI) ion source of the mass spectrometer. The ion source was operated at 70 eV. The injection port, transfer line and ion source temperature were set at 300, 300 and 230 °C, respectively. The separated peaks were identified using a Wiley NIST MS Library and F-Search (ver. 1.11, Frontier Lab).

ESI-MS. The ESI-MS experiments were performed on an LCQ DECA XP MS spectrometer (Thermo Finnigan, San Jose, CA) equipped with an electrospray ion source. All of the ion trap analyzer parameters were optimized according to the manufacturer's instructions. The spray voltage was -4 kV in negative mode under an N₂ sheath gas flow at 50 arbitrary units. The capillary temperature was maintained at 275 °C. To obtain the ESI mass spectra of the PR and used stripper, the samples diluted with tetrahydrofuran (THF) (1:1) were directly introduced into the ESI source with a mobile phase consisting of water/acetonitrile (50:50) containing 0.1% formic acid with a pump at 50 μ L/mL. Total ion chromatograms from m/z 150 to 2000 were obtained. For the MS/MS

experiment, the maximum ion injection time, activation time, and isolated ion width were set to 500 ms, 30 ms, and 2.0 u, respectively. The collision energy with helium was set to 35% of the radio frequency (5 V) applied to the ion trap analyzer.

Results and Discussion

Analysis of stripper solutions by GC/MS. In general, the stripper solution used in the processing of TFT-LCDs contains an organic amine to reduce the attraction between the coated polymer and substrate, a protonic polar solvent to prevent the volatilization of the stripper in order to maintain its composition, and a non-protonic polar solvent to dissolve the stripped polymer. The types and composition of the compounds in the stripper vary according to the preparation method of the manufacturer. In order to obtain information on the stripper solution used in this study, a GC/MS analysis was preformed. The total ion chromatogram (TIC) of the stripper is shown in Fig. 1a. The two major peaks, 1-methyl-2-pyrrolidone (NMP) at 3.78 min and 2-(2-butoxyethoxy) ethanol (BDG) at 5.75 min, correspond to the non-protonic polar solvent and protonic polar solvent used in this stripper, respectively. In addition, the peaks for 1,2-ethanediol at 1.70 min and 2-aminoethanol at 2.88 min as minor additives were confirmed by the interpretation of their mass spectra based on a library search.

During the stripping process of TFT-LCD production, the PR coated on the substrate is stripped and accumulated in the stripper solution. The PR comprises mainly a polymer resin, photo active compound (PAC), and sensitivity promoter, which cannot be discriminated using the conventional GC/MS technique due to their low volatility and low level in the stripper. Thus, the TIC of the used stripper shows the same peaks as those of the original stripper, except for the peak of 2-aminoethanol which is observed in the unused stripper but not in the used stripper (Fig. 1b).

Analysis of minor polymer and residues in used stripper by Py-GC/MS. The Py-GC/MS method has sometimes been used to identify non-volatile and high molecular weight polymers through their monomer or pyrolysate.^{25,26} However,

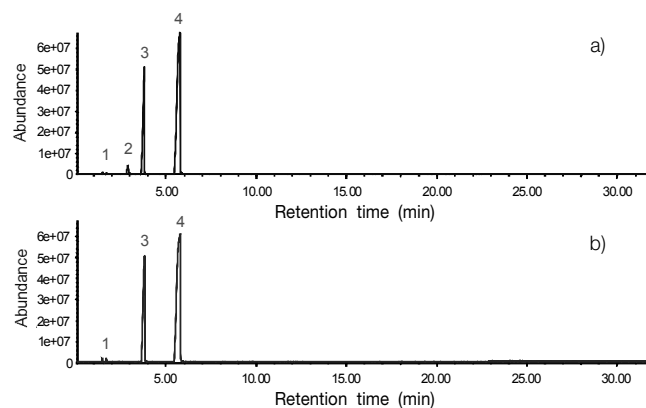


Figure 1. Total ion chromatograms (TICs) of a) stripper and b) used stripper solution obtained by GC/MS. Peak identities as follows; (1) 1,2-ethanediol, (2) ethylamine, (3) 1-methyl-2-pyrrolidone, and (4) 2-(2-butoxyethoxy)ethanol.

Table 1. Characteristic pyrolysates of stripper, photoresist, and used stripper solution produced by Py-GC/MS at 500 °C

No.	compounds	MW (Da)	R.T. (min)	stripper	photoresist	used stripper
1	morpholine	87	1.95	O		O
2	indene	116	3.69		O	
3	<i>m</i> -and <i>p</i> -cresol	108	3.93		O	O
4	di-methylphenols	122	4.7-5.6		O	O
5	benzoic acid	122	5.49	O		O
6	tri-methylphenols	136	5.6-7.2		O	O
7	2-phenyl-2-oxazoline	147	7.42	O		O
8	tetra-methylphenols	150	7.5-8.0		O	
9	di-benzoyl-aminoethanol	269	14.50	O		O
10	methylenebis(methylphenol)	228	16.2-17.9		O	O
11	methylenebis(di-methylphenol)	256	17.3-18.3		O	O

pyro-products resulting from the thermal decomposition are produced through diverse mechanisms, so that their origins may not be entirely comprehended when an unknown or mixed sample is pyrolyzed. Most of the impurities in the used stripper may be the PR components, and in order to distinguish the pyro-products of the PR from those of the original stripper in the pyrogram of the used stripper, the pure stripper and PR need to be pyrolyzed individually to validate the detection method of the trace PR.

The analysis of the used stripper containing the PR and other impurities can be simplified by employing subsequent temperature steps to reduce the peaks resulting from the volatile stripper. Accordingly, the Py-GC/MS analysis of each sample was performed with thermal desorption at 300 °C in order to allow the major volatile compounds in the stripper to be desorbed by the heating of the sample. The subsequent pyrolysis of the residue at 500 °C could reduce worthless peaks related to the major stripper solvent.

Fig. 2a shows the pyrogram obtained from the new stripper solution. The three major pyrolysates produced from the residual stripper after its thermal desorption were identified as morpholine at 1.95 min, 2-phenyl-2-oxazoline at 7.42 min, and dibenzoyl-aminoethanol at 14.50 min. The dibenzoyl-aminoethanol may be produced by the condensation of two benzoic acids and a 2-aminoethanol. This is supported by the presence of benzoic acid at 5.49 min in the pyrogram and 2-aminoethanol at 2.88 min in Fig. 1a which is an additive added as a corrosion inhibitor. Peaks 1 and 7 were assumed to be the pyrolysates produced from NMP, but their mechanisms could be not understood entirely.

The pyrolysis of the PR revealed the structure of the polymer resin, which was possible to interpret with the mass spectra of the pyro-products. Novolac as the polymer resin of the PR is formed from the reaction of *meta*- and *para*-cresol with formaldehyde under acid catalyzed conditions,²⁷ and the initial reactants produced by pyrolysis are observed at 3.93 min corresponding to the cresol peak (Fig. 2b). This is because the two isomers are not separated on the non-polar column due to their similar chromatographic behavior.^{28,29} Additionally, the pyro-products produced by the methylation, di-methylation and tri-methylation of the cresols during the thermal reaction were observed as di-methylphenols, tri-methylphenols and tetra-methylphenols, respectively, at between 4.7

min and 8.0 min. Dimers formed by the thermal cracking of novolac, viz methylenebis(methylphenol) isomers, are also observed at longer retention times of 16.2 min to 17.9 min. The methylation and di-methylation of the dimers may have occurred at the phenyl group during the pyrolysis of the PR and, as a result, methylenebis(di-methylphenol) isomers were observed at 17.3 min to 18.3 min. The chemical structures of the pyrolysates produced from novolac by pyrolysis are shown in Fig. 3. Indene, which is a pyrolysate resulting from PAC, an additive of the PR, is also indicated at 3.69 min.

A pyrogram of the used stripper is shown in Fig. 2c., in which the peaks seem to be merged with those of the original stripper and PR, although the relative intensity of the peaks is different. In the used stripper, the presence of the residue PR was identified by the peaks of the cresols, di-methylphenol, tri-methylphenol, methylenebis(methylphenol) and methylenebis(di-methylphenol) isomers. The representative peaks of novolac may be used as indices of the PR in the used stripper (Table 1).

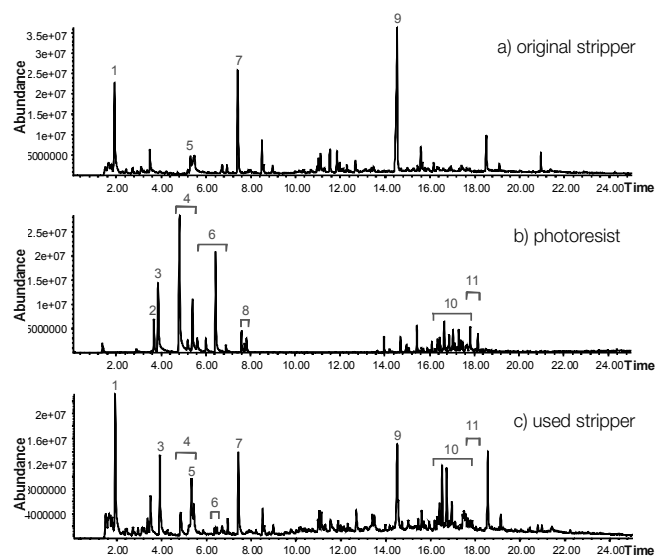


Figure 2. Pyrograms of a) original stripper, b) photoresist, and c) used stripper solution produced by Py-GC/MS at 500 °C. Peak identities as follows; (1) morpholine, (2) indene, (3) *m*- and *p*-cresol, (4) di-methylphenols, (5) benzoic acid, (6) tri-methylphenols, (7) 2-phenyl-2-oxazoline, (8) tetra-methylphenols, (9) di-benzoyl-aminoethanol, (10) methylenebis(methylphenol)s, and (11) methylenebis(di-methylphenol)s.

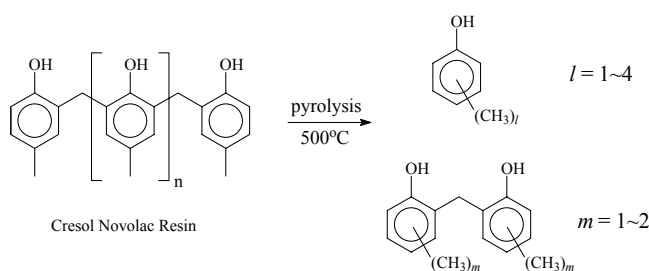


Figure 3. Chemical structures of pyrolysates produced from novolac by pyrolysis at 500 °C.

Structural analysis of the polymer in the used-stripper by ESI-MS. As described in the previous section, Py-GC/MS is a useful analytical tool to discriminate the trace PR components from the used stripper solution. However, the pyrolysis did not provide information on the structure of the intact polymer, but only the thermal degraded products that are dependent upon the structure and bond dissociation energies of the polymer and additives. The products identified by the mass spectra provided information on the presence of the PR, whereas the chemical structure of the backbone and functional groups of the polymer were not revealed. Electrospray ionization (ESI) as a soft ionization technique allows intact polymer ions to be generated with little or no fragmentation.^{30,31} Accordingly, the ESI-MS technique was applied to analyze the structure of the novolac polymer in the used stripper deduced from the Py-GC/MS results.

The mass spectrum obtained by direct ESI-MS in negative ion mode of the PR by infusion is shown in Fig. 4a. The spectrum reveals the distribution of the deprotonated oligomer ions $[M_n-H]^-$ with $n=0\sim14$. No multiple charged oligomer peaks created by ESI were observed under our experimental conditions. The average molecular mass in the ESI mass spectrum is about m/z 820, which may be different from the average molecular weight due to the discrimination in the mass response. The repeat mass differences of 120 Da between the cluster ions indicate that the chain unit of the oligomers is di-methyl phenol. The observation of di-methyl phenols as the major pyrolysate in Fig. 2b also suggests that it is the repeat unit of novolac. Additionally, three or four distinct ions in each cluster, for instance m/z 827.7, 841.7 and 855.7 of the most abundant cluster, are observed at regular intervals of 14 Da, probably resulting from methylation or di-methylation to the novolac oligomer at m/z 827.7.

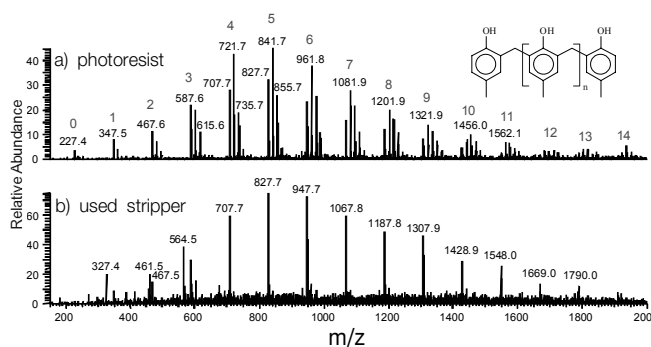


Figure 4. Full-scan negative ion mass spectra of a) photoresist and b) used stripper obtained by ESI-MS.

Identification of various di- and tri-methyl phenols in Fig. 2b proves that the repeat chains of these oligomers were modified with the CH_3 group.

Tandem mass spectrometry (MS/MS) was employed to obtain further structural information on the synthetic polymer in the PR. The 5-mers of the novolac cluster were chosen for this study. The ESI-MS/MS spectrum of the precursor ion of m/z 827.4 is shown in Fig. 5a. Fragment ions produced by the bond cleavages of the methylene bridges between phenyl groups are dominant. The ion series corresponding to the losses of a methylphenol and a di-methylphenol group from the end group of novolac are observed at m/z 719.3 and 707.3, respectively. The possible fragment ions produced by the cleavage of the novolac are depicted in Fig. 5 as an inset. The fragment ions caused by the sequential loss of 120 Da up to $n=2$ from $n=5$ revealed that the repeat unit of the oligomer is di-methylphenol. In the MS/MS spectrum of m/z 841.4 (Fig. 5b), the mass differences of 108, 120, and 134 Da from the precursor ion may provide information on the cleavage of methylphenol, di-methylphenol and tri-methylphenol, respectively. These inferences would be supported by the observation of fragment ions produced by the loss of ethylphenol for 120 Da, and propylphenol or methylethylphenol for 134 Da, but these compounds were not observed in the Py-GC/MS results. Therefore, it can be deduced that these are not the fragment ions. If the methylated site is only positioned at the repeat unit of $n=5$, the fragment ions corresponding to $n=4$ must be equal to those in Fig. 4a, such as those at m/z 587.2 and 599.3. However, the observation of two additional productions at m/z 601.3 and 613.3 suggests that the methylation at the repeat unit is present at position $n=4$, but not $n=5$. The observation of the four fragment ions of the repeat units informs us that the di-methylphenol produced by the methylation of methylphenol during the synthesis of novolac is randomly located in the repeat unit of the 5-mer corresponding to m/z 841.4. The same interpretation can be made to the MS/MS peaks generated at m/z 855.4 (Fig. 5c), where two

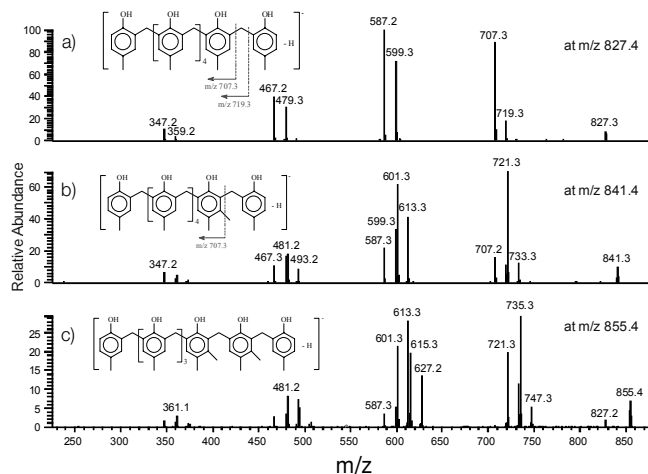


Figure 5. MS/MS spectra produced from a) m/z 827.4, b) m/z 841.4, and c) m/z 855.4 indicated in Fig. 4a. The chemical structures inserted in b) and c) are only depicted the 5-mer modified with di-methylphenol in $n=4$, and $n=4$ and 5, respectively, although the di-methylphenols are randomly located in the repeat units of novolac.

methylation sites in the repeat unit also exist randomly in the polymer molecule.

The used stripper solution shows polymer peaks in the ESI spectrum of Fig. 4b, although their intensities are relatively low compared to those of the PR, due to the small amount of novolac. Particularly, all of the novolac oligomers constituted of the repeat unit of di-methyl phenol do not show any modification by methylation in the repeat unit. These results indicate that the oligomers modified with methyl and di-methyl groups occur as a result of a chemical change which takes place during the lithography using ultraviolet light or that it is difficult to remove the methylated novolac on the substrate during the stripping process. The peaks not associated with the oligomer in Fig 4b, viz. the m/z 327.4, 461.5 and 564.5 ions, were considered to be peaks arising from the stripper solution. However, the peaks were not the major compounds of stripper which were confirmed with each standard using ESI-MS. They may be trace components in stripper, but identification of them was not carried out in this study. This ESI analysis provided the structure of the trace novolac remaining in the used stripper without any sample treatment.

Conclusion

The Py-GC/MS method provided the means to confirm the existence of PR as a minor constituent in used stripper, whereas application of the conventional GC/MS method was limited to determining the major solvent components in the stripper solution. The analysis of the used stripper by gas phase reaction at high temperature produced various pyrolysates. Nevertheless, the trace components such as additives and polymers were distinguished from those of the stripper solution by comparing the pyrograms of the new stripper and the PR. The structure of the novolac used as a polymer in the PR was confirmed with the observation of the methyl phenol, di-methyl phenol and methylenebis(methyl-phenol) isomers corresponding to the monomers, methylated monomers and dimers of the novolac, respectively. The analysis of the used stripper by ESI-MS also provided structural information on the residue polymer. The intact oligomers of the PR of up to 14-mer were composed of three types of polymers, viz. the normal, methyl, and di-methyl novolac. The detailed structures of their repeat chains and ending groups were revealed by the fragment ions observed using the MS/MS technique. The results indicated that the methylated and di-methylated positions are distributed randomly in the repeat unit. However, the novolac present as an impurity in the used stripper solution was detected as an oligomer mixture containing only the non-modified backbone. By the combination of Py-GC/MS

and ESI-MS, the determination and structural information of the non-volatile impurities, especially the polymer, in the used stripper were achieved.

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