POLYSULFONE WITH LOWER LEVELS OF CYCLIC DIMER : USE OF MALDI-TOF IN THE STUDY OF CYCLIC OLIGOMERS

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Abstract

Solutions of Polysulfone in certain solvents can become cloudy due to a slight and partial precipitation of a cyclic oligomer, which has been characterized to be crystalline cyclic dimer of Polysulfone containing two repeat units of Polysulfone. This precipitation has been a source of manufacturing problems in a number of solution processing industries such as membranes, films and coatings. MALDI-TOF Mass Spectroscopy was successfully employed to establish the presence of not only cyclic dimer but also other cyclic oligomers such as trimer, tetramer, pentamer, hexamer and so on in commercially available polyarylsulfones. Solvay Advanced Polymers has developed a proprietary process for making Polysulfone with lower levels of cyclic dimer and other cyclic oligomers. This commercially available low cyclic dimer Polysulfone resin offers a number of advantages to the solution processing industries such as long self-life, and less insoluble material that needs to be filtered. Reduction in cyclic oligomeric content also fortuitously reduced the polydispersity of the resin. For a given weight average molecular weight, increased number average molecular weights have been obtained for the low cyclic dimer resin which is expected to increase the mechanical properties of the membranes.

Keywords: polysulfone, cyclic dimer, cyclic oligomer, MALDI-TOF, membranes, molecular weights

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INTRODUCTION

Polyarylsulfones are high performance thermoplastics with such desirable characteristics as solubility in water-soluble solvents, ability to form various types of membranes, resistance to cleaning chemicals such as acids/bases and chlorine, and sterilizabilty. UDEL® Polysulfone has been a preferred membrane resin for applications involving kidney dialysis, water and waste water purification, desalination and gas separation. In general, membrane manufacturing processes involve contacting a solution of Polysulfone with a non-solvent such as water in a precisely controlled manner in the desired physical form such as hollow fiber or flat-sheet. The use of water as non-solvent requires the polymer solvent to be miscible in water. Concentrated solutions of polysulfone in solvents such as dimethylformamide, dimethylacetamide, and Nmethylpyrrolidinone provide clear and viscous solutions, but they may, depending on conditions, become cloudy over a period of time. This cloudiness could be removed by filtration and was identified to be crystalline cyclic dimer of polysulfone (Figure 1). [1, 2] These results seem to suggest that all of the cyclic dimer initially present is soluble and over time, a part of this soluble cyclic dimer slowly crystallizes to impart haziness to these solutions.

The cyclic dimer is made during the polymerization and polysulfone resin was found to contain 1.5 weight % cyclic dimer by Size Exclusion Chromatography. In membrane manufacturing processes such precipitation of cyclic dimer results in scale in storage vessels, and pipes and is partly responsible for increased usage of filters due to clogging. Unfiltered crystalline dimer may also lead to imperfections on the surface of the membrane. The crystalline residues once formed cannot be dissolved readily in the solvents from which the crystallization occurred and thereby create challenges for cleaning the process equipments.

We report herein the evidence for the presence of other cyclics such as trimer, tetramer etc in commercially available polyarylsulfones. We also report commercial availability of UDEL® Polysulfone with lower levels of cyclic oligomers that are more suitable for solution processing industries.

EXPERIMENTAL

Size Exclusion Chromatography (SEC) was performed on two 5µm mixed-D Size Exclusion Chromatography (SEC) columns from Polymer Laboratories using a polymer solution dissolved in methylene chloride. An ultraviolet detector at a wavelength of 254 nm is used to obtain the chromatogram. Waters GPC or LC software is used to measure the areas for the cyclic dimer (CD) peak and for the whole polysulfone and the weight percent cyclic dimer is calculated from the ratio of these areas. The assumption is made that the detector response for the cyclic dimer is similar to that for the whole polymer. To ensure reproducible CD % levels, a standard polysulfone sample is analyzed with the samples and, based on the standard's result and its expected value, a correction is made to allow for the day-to-day variation of the analysis.

MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI-III in reflectron high power mode at a wave length of 337 nm (N_2 laser light). Dithranol was used as a matrix and the polymer samples were dissolved in 1,1,2,2-tetrachloroethane (TCE). Lithium bromide or silver trifluoroacetate in tetrahydrofuran was used as ionization promoter.

RESULTS AND DISCUSSION

During UDEL® Polysulfone manufacture, a slight precipitation may occur and this precipitate has been characterized to be cyclic dimer of Polysulfone by High-resolution mass spectroscopy, ^1H NMR, end-group analyses and Size Exclusion Chromatography. We did not know whether other cyclic oligomers such as trimers, tetramers etc existed in UDEL® Polysulfone. The existence of macrocycles in polysulfone has been reported recently in the literature. [3, 4] It has also been reported that a ring-chain equilibrium exists when aromatic polyethers are heated in the presence of CsF and under these conditions the content of macrocyclic oligomer is concentration dependent.

[5] Also several groups have reported on the selective syntheses of cyclic ethersulfones. [6-9] We have employed MALDI-TOF Mass Spectroscopy that showed evidence for the presence of other cyclic oligomers in commercially available polyarylsulfones such as Polysulfone and Polyphenylsulfone. A purified sample of UDEL® Polysulfone cyclic dimer was employed as a standard for MALDI analysis. This purified sample was obtained from Polysulfone manufacturing and was recrystallized from dichlorobenzene. It showed a peak at a molecular weight of 890.4 compared with the expected peak is at 891.9 for the dimer with a lithium ion. Notably, this spectrum showed absence of any other oligomeric species showing that this is a pure sample and hence indicating that no other species in UDEL® Polysulfone has a tendency to crystallize. A very dilute solution of commercially available UDEL® Polysulfone pellet provided the MALDI results shown in Table 1. As expected, the cyclic dimer is present in the spectrum. The other major peaks are found to be separated by the repeat unit molecular weight of approximately 442. The observed molecular weights for these peaks coincide with the calculated molecular weights of cyclic trimer, tetramer, pentamer, hexamer and heptamer. Figure 2 shows the MALDI spectrum for UDEL® Polysulfone up to 4000 molecular weight. Higher cyclic oligomers than heptamer were present at much lower and progressively decreasing concentration. Also important is the fact that linear oligomers are found at much lower concentrations than cyclic oligomers and this fact is consistent with their disappearance due to their reactivity during polymerization as compared to cyclic oligomers and due to the high extent of reaction required to make the Polysulfone P-3500 grade.

It was thought that polysulfone with reduced levels of cyclic dimer would slow the crystallization process and hence allow the solutions of polysulfone to remain clear for longer periods of time. An economically viable process involves reduction of cyclic dimer during the synthesis of polysulfone rather than its removal from already manufactured polysulfone. Using a proprietary process, Solvay Advanced Polymers has developed two new grades of UDEL® Polysulfone, P-3500 LCD and P-1700 LCD with lower cyclic dimer levels for use in solution processing industries. These commercially available grades contain less than 1.20% cyclic dimer. Figure 3 shows an SEC trace of UDEL® Polysulfone whereas Figure 4 shows an expanded view of the oligomeric region. The last peak on the trace has been proven to be that of cyclic dimer by comparison to an authentic sample. In view of the MALDI results, the peaks left to the cyclic dimer peak are considered to be other cyclic oligomers such as trimer, tetramer etc. Figure 4 clearly shows that the LCD grade contain lower amounts of cyclic oligomers.

We have found that the precipitation of cyclic dimer is non-linearly proportional to the concentration of the cyclic dimer. This qualitative study involved visual observation for cloudiness in the solutions containing Polysulfone and polyvinylpyrrolidinone. Table 2 shows the results of this study. A solution of a polysulfone (18%) and polyvinylpyrrolidinone (5%) in DMAC at 40^{o}C that contained 1.5% cyclic dimer became cloudy in a few days whereas a resin with 1.25% cyclic dimer remained clear for 30 days. Cyclic dimer precipitation is also dependent on the temperature of the polysulfone solution. Tests at 75^{o}C showed that clarity of the solutions can be maintained for more than two months when the cyclic dimer levels are lower.

Solvay's proprietary process for reducing cyclic dimer also reduced other cyclic oligomers. A fortuitous effect of this reduction is to increase the number average molecular weight for a given weight average molecular weight. Table 3 shows the cyclic dimer and molecular weighs obtained by SEC. Both P-3500 LCD (Low Cyclic Dimer) and P-1700 LCD grades show about 10% improvement in number average molecular weights.

Membrane manufacturing with LCD Polysulfone is expected to offer a number of process and product advantages. We expect that reduced precipitation during membrane manufacturing to contribute to longer runs and reduced use of filters. We also expect that imperfections on the surface of the membrane created by unfiltrable crystalline cyclic dimer to decrease and this might improve process yields and/or performance of the membrane. We also expect the mechanical properties of the membrane to improve due to the higher number average molecular weight of the LCD grade. Increased mechanical properties can result in lower fiber breakages during manufacture.

CONCLUSIONS

We speculate that many condensation polymers that are assumed to contain linear polymer molecules, in general, may contain oligomeric cyclic polymer molecules and perhaps even macrocyclic molecules. Reduction of cyclic dimer in UDEL® Polysulfone results in improvement in number average molecular weight. Commercially available LCD grades from Solvay are better suited for solution processing industries.

Figure 1. Polysulfone cyclic Dimer

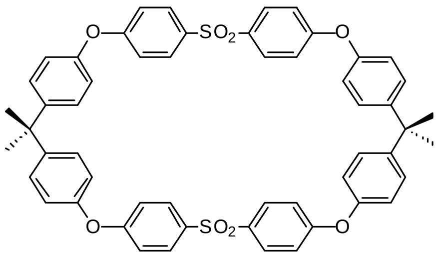


Table 1. Polysulfone MALDI Results

Species	Calculated MW	MALDI MW
Cyclic-4-mer + Li	892.1	891.9
Cyclic-6-mer + Li	1334.6	1336
Cyclic-8-mer + Li	1777.2	1778.6
Cyclic-10-mer + Li	2219.7	2223.2
Cyclic-12-mer + Li	2662.2	2667.0
Cyclic-14-mer + Li	3104.8	3108.8

Figure 2. Polysulfone MALDI Spectrum

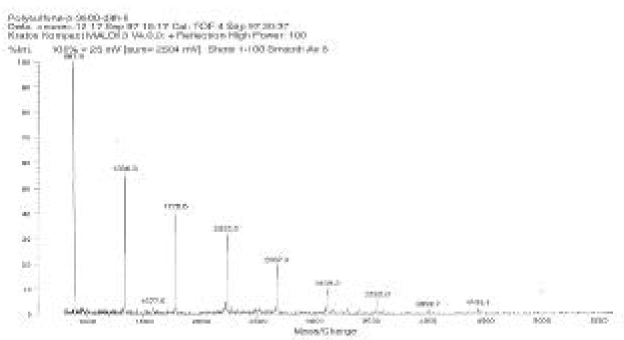
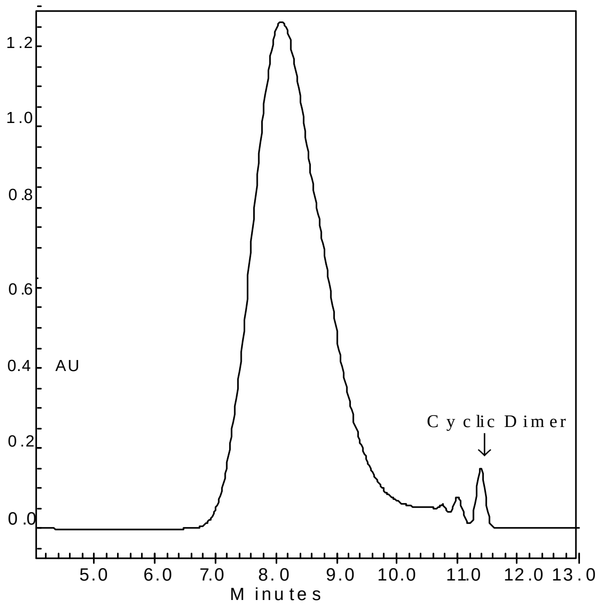


Figure 3. SEC Trace of UDEL Polysulfone

Figure 4. Expanded View of the Oligomeric Region of Polysulfone



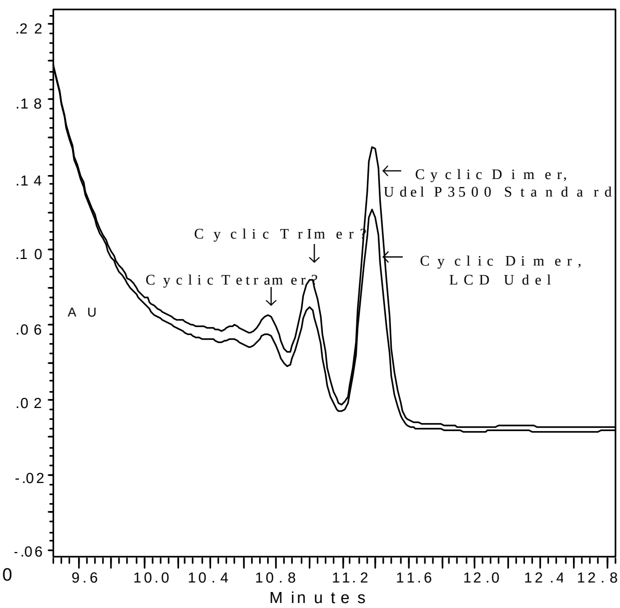


Table 2: Number of Days for Cloudiness to Develop in PSF (18%) and PVP (5%) Solutions in DMAC

CD%	Number of Days	Temperature(C)
1.50	Cloudy In 5 days	40
1.34	Cloudy In 5 days	40
1.25	Cloudy In 30 days	40
1.00	Clear on 60 th day	40
1.50	Cloudy In 2 days	75
1.34	Clear on 60th day	75
1.25	Clear on 60th day	75
1.00	Clear on 60th day	75

Table 3: Comparison of Molecular Weights of Polysulfones with different CD Levels

Grade	CD%	Mw	Mn	Mw/Mn
P-3500 LCD	1.09	73704	22033	3.35
P-3500 LCD	1.08	75909	22296	3.40
P-3500	1.50	76947	20270	3.80
P-3500	1.50	77875	19905	3.91
P-1700 LCD	1.06	69798	21866	3.19
P-1700 LCD	1.05	68854	21738	3.17
P-1700	1.50	65882	18629	3.54
P-1700	1.50	66909	18777	3.56

REFERENCES

1. J.G. Wumans and C.A. Smolders, Removal of low molecular weight, crystalizable polymer fraction from solutions of poly(oxy-1,4-phenylenesulphonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene) (Polysulfone®), Eur. Polym. J. 12 (1983), 1143-1146.

2. H.M. Colquhoun and D.J. Williams, Isolation and structural characterization of the macrocyclic dimer present in bisphenol-A Polysulfone, Macromolecules, 29 (1996) 3311-3314.

3. H.R. Kricheldorf, S. Bohme, G. Schwarz, R-P. Kruger and G. Schulz, Macrocycles 18. The role of cycliczation in syntheses of poly(ether sulfone)s, Macrocycles, 34 (2001) 8886-8893.

4. D. Vitalini, P. Mineo and E. Scamporrino, Further application of a procedure for molecular weight and molecular weight distribution measurement of polydisperse polymers from their matrix-assisted laser desorption/ionization time-of-flight mass spectra, Macromolecules, 30 (1997) 5285-5289.

5. A. Ben-Haida, I. Baster, H. M. Colquhoun, P. Hodge, F. H. Kohnke and D.J. Williams, Ring opening depolymerization of aromatic polyethers, Chem. Commun., 1997, 1533-1544.

6. T.E. Atwood, D.A. Barr, T. King, A.B. Newton and J.B. Rose, Polymer, 18 (1977), 359.

7. M.J. Mullins, E.P. Woo, D.J. Murray, and M.T. Bishop, Chemtech, 1993, 25.

8. D.Xie and H.W. Gibson, Macromolecules, 30 (1997), 4814.

9. Y. Qui, N. Song, T. Chen, S. Bo and J. Xu, Macromol. Chem. Phys. 201 (2000), 840.