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Thermal degradation of chemically modified polysulfones☆

Gábor Molnár, András Botvay*, László Pöppl✠, Kornél Torkos, József Borossay†, Árpád Máthé, Tünde Török

Institute of Chemistry, Eötvös Loránd University, H-1518 Budapest 112, PO Box 32, Hungary

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Abstract

The thermal stability of some known (bromomethylated, carboxylated, brominated, nitrated) and novel (tertiary amine) polysulfone (PSU) derivatives has been studied by thermogravimetry (TG). The thermal decomposition products have been identified by various coupled mass spectrometric (MS) methods. From these data, the possible decomposition mechanism was deduced.

Keywords: Polysulfone derivatives; Thermal stability; Thermal degradation; Thermogravimetry; Mass spectrometry

1. Introduction

Aromatic polysulfones are a family of amorphous, thermoplastic engineering polymers with phenylene, sulfone, ether, and in some cases, other groups in the main chain. They possess remarkable thermal and chemical stability, excellent strength and flexibility, as well as high glass transition temperature and good film-forming properties. In addition to several technical applications, they are mainly important as they give high-quality semipermeable membranes. Despite these benefits, however, polysulfone membranes have also some disadvantages in practical uses, such as their rather hydrophobic nature. For this reason, there is a high interest in the chemical modification of polysulfones.

Beyond hydrophilization, various chemical modifications afford the possibility of introducing ionic and other special functionalities onto the polymers in order to tailor their membrane separation characteristics and enlarge the scope of their use. Among these polymers, Udel type polysulfone (PSU, Fig. 1) seems to be the most suitable for functionalisation, at the same time being the most widespread as well. (Details about the synthesis and characterization of this base polymer can be found in Ref. [1].) The aromatic rings of its bisphenol A moiety ($-O-Ph-C(CH_3)_2-Ph-O-$) are activated for electrophilic substitution *ortho* to the ether linkage. On the other hand, the *ortho*-sulfone position can be lithiated, and the resulting intermediate is reactive to a variety of electrophiles providing excellent synthetic pathways for numerous functional groups [2]. Indeed, a number of derivatives, such as sulfonated, nitrated, halomethylated, and carboxylated PSU, have been prepared. (A detailed survey of PSU modifications is given in Ref. [3].)

While these substituents bring about improved or novel separation (i.e. physico-chemical) properties, they modify the thermal behaviour of the original polymer as well. Thermal degradation processes of unmodified

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☆ This paper is dedicated to the memory of our deceased colleagues by the other co-authors.

* Corresponding author. Tel.: +36 1 2090555; fax: +36 1 2090602. *E-mail address:* botvay@para.chem.elte.hu (A. Botvay).

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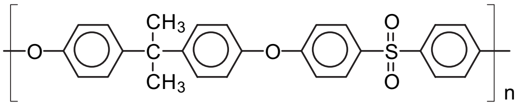

Fig. 1. Structural unit of Udel PSU.

polysulfones have been extensively studied since their discovery [4–10], and considerable efforts have recently been made to reveal the thermal behaviour of chemically modified PSU [11–22]. In this paper, we report on the preparation of some new tertiary amine substituted polysulfones, as well as on the thermal degradation of these and some other PSU derivatives.

The thermal decomposition mechanism of a polymer chain can be often deduced from the pyrolysis products formed. Under this aspect, the identification of the degradation products by coupled mass spectroscopic (MS) methods yields unique information. In this study we used three different MS methods: direct pyrolysis–mass spectrometry (DP–MS), thermogravimetry coupled with mass spectrometry (TG–MS) and pyrolysis–gas chromatography coupled with mass spectrometry (P–GC–MS).

All these techniques have their own advantages and drawbacks. DP–MS is specific in that the pyrolysis is achieved under high vacuum, at the microgram level and adjacent to the electron emitter. Therefore, it allows the detection of primary degradation products before they could undergo further degradation, and of ions of high mass. Unfortunately, the resulting mass spectra contain mixed information on the products and therefore the identification of the individual compounds is rather difficult, especially when no soft ionisation (chemical ionisation, etc.) method is available, as in our case. P–GC–MS displays quite the opposite characteristics, i.e. long residence and transport time in more or less hot zones that may lead to further decomposition of labile primary products and/or to condensation of heavy fragments before they could reach the detector. On the other hand, mass spectra of each compound can be analysed. In contrast, TG–MS is relatively disadvantageous in that residence and transport times are long compared to DP–MS and the spectral information is often complex. However, this is the only method that permits analysis of the different decomposition steps during the thermal cycle. In summary, it turns out that a comparative study using these complementary techniques can be advantageous.

2. Experimental

2.1. Materials

The basic polymer used was commercial Udel polysulfone (P-1700, Amoco Performance Products, Inc.) with the structural unit shown in Fig. 1. It was dried at 150 °C for 3 h prior to reaction. The various reagents and solvents employed in the preparation of the derivatives were of analytical grade purity.

2.1.1. Synthesis

Bromination [11], carboxylation [12], bromomethylation [16] and nitration [21] of polysulfone have been performed by standard methods described in the literature. Some new tertiary amine derivatives have been prepared from bromomethylated polysulfone (PSU–CH_2Br) by reacting it with different secondary amines (*N*-methylaniline, *N*-ethylaniline, *N*-propylaniline, *N*-phenylaniline (= diphenylamine)). Except the case of *N*-Me-aniline, the reagents and the polymer were dissolved in dimethyl formamide (DMF). The reaction mixture was kept at reflux temperature (~152 °C) for 6–8 h (depending on the amine), then the polymer was precipitated and washed with methanol and finally dried in a vacuum desiccator. Since *N*-Me-aniline dissolves PSU–CH_2Br no extra solvent was used in this case, and the reaction mixture was kept at reflux temperature (~127 °C) for 2 h.

2.1.2. Characterization

The modified polymers were characterized mainly by elemental analysis. Br content was determined by the Schöniger method, while N% was measured using a Heraeus Rapid CHN-Automat apparatus. The degree of substitution (DS) was calculated (Table 1) from these data except PSU–COOH whose DS was determined from the TG analysis (see later).

The structures of PSU–Br [11], PSU–COOH [12], PSU–CH_2Br [16], and PSU–NO_2 [21] (see Fig. 2) had been verified by NMR or IR spectroscopy. In case of the amine derivatives, we could ascertain by elemental analysis that the bromomethyl groups had been quantitatively transformed and *N*-containing groups had been attached to the polymer.

Table 1
Degree of substitution (DS) of the investigated polysulfone derivatives

Sample	DS
PSU–Br	2.22
PSU–CH_2Br	1.36
PSU–NO_2	0.52
PSU–COOH	0.7[a]
PSU–CH_2NPhMe	1.30[b]
PSU–CH_2NPhEt	0.75[b]
PSU–CH_2NPhPr	0.75[b]
PSU–CH_2NPh_2	0.75[b]

[a] From thermogravimetric analysis.

[b] The product contained no Br, but contained N; the DS was taken to be equal to that of the starting PSU–CH_2Br.