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FUNCTIONAL POLYAMIDES: 4. SYNTHESIS AND CHARACTERIZATION OF POLY(AMIDE-SULFONES)

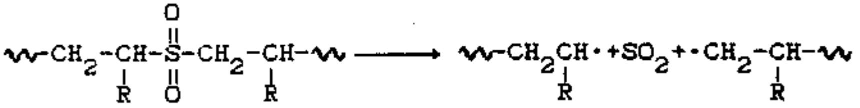
Selcuk DENIZLIGIL, Niyazi BICAK, and Yusuf YAGCI
Istanbul Technical University
Department of Chemistry
Maslak, Istanbul 80626, TURKEY

ABSTRACT

Condensation of β,β'(ethylenedisulfone)dipropionitrile (EDSP) and cocondensation of mixtures of EDSP and different amounts of adipoyldinitrile with formaldehyde in the presence of sulfuric acid were carried out to yield polyamides with sulfone groups. Incorporetion of adipoyl segments improved solubility and crystallinity of the polyamide sulfones(PAS). Thermal stabilities of PASs were also studied by thermogravimetric analysis.

INTRODUCTION

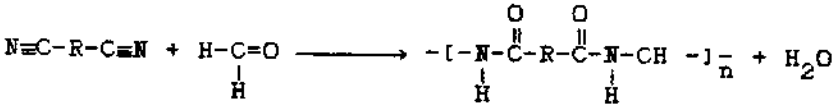
During recent years polymers containing sulfone groups have attracted attention for their applicability for technichal processes such as electron resist [1]. This class of polymers was found to exhibit rather high radiation sensitivity in terms of main-chain scission. Upon high energy radiation, C-S bonds are split and spontaneous extrusion of sulfur dioxide occurs [2,3].



$$\sim CH_2-\underset{R}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_2-\underset{R}{\underset{|}{CH}}-\sim \longrightarrow \sim CH_2\underset{R}{\underset{|}{CH}}\cdot + SO_2 + \cdot CH_2-\underset{R}{\underset{|}{CH}}-\sim \quad (1)$$

More recently, Reddy and Srinivasan [4] prepared heat-resistant aromatic polyamides prossesing sulfone groups in the main chain. Introduction of these groups greatly improved the solubility properties of the polyamides without the loss of thermal stability.

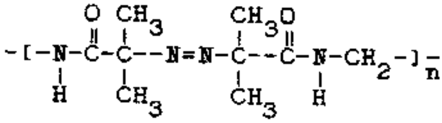
In addition to this classical methods, polyamides can be prepared [5] by the low temperature solution method by condensing dinitriles with formaldehyde in the presence of strong acid such as sulfuric acid or formic acid according to the following reaction.



$$N\equiv C-R-C\equiv N + \underset{H}{\underset{|}{H-C}}=O \longrightarrow -[-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH-]_n + H_2O \qquad (2)$$

Our own studies on the functional polyamides were directed towards the synthesis of these polymers by selecting structurally suitable R group (reaction 2).

In a previous paper [6], we synthesized a polymeric azo initiator from formaldehyde and the well known azo initiator 2,2'-azobis(isobutyronitrile) (AIBN) The resulting polyamide with the following structure,



$$-[-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-N=N-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH_2-]_n$$

was used to prepare block copolymers by sequential decomposition [7]. More recently, we have reported [8] the synthesis of polyamide containing thioether groups using the correspondig dinitrile with formaldehyde under similar conditions. The obtained polyamides were shown to coordinate mercury with a high degree of selectivity.

The aim of the present paper is to synthesize poly(amide-sulfones) (PAS) using sulfone dinitriles. We set different reaction conditions i.e. addition of various molar ratios of adipoyl dinitrile, to improve the solubility properties of the resulting polyamides.

EXPERIMENTAL

Materials

Trioxane (Aldrich) was recrystallized from diethylether. Adipoyldinitrile (Fluka) was used without further purification . Dioxane was purified according to conventional drying and distillation procedures. β,β'(etylenedithiol)dipropionitrile (EDP) was obtained by method described earlier [7].

Preparation of β,β'(ethylenedisulfone)dipropionitrile (EDSP)

EDP (3.78 mmol) was dissolved in 20 ml dioxane at room temperature and 4 ml of hydrogen peroxide (30%) was then added dropwise in 10 min. The reaction mixture was stirred overnight. The product precipitates after standing in a refrigerator was filtered off. The product was further purified by recrystallization from dioxane (Yield 64.6%, mp.127 °C as determined by DSC).

Polyamide Synthesis from EDSP and Trioxane

A typical low temperature polycondensation is described below.

Trioxane (0.12 mmol) was dissolved in a given amount of 95% sulfiric acid and 0.38 mmol EDSP was added with stirring over a period of 10 minutes at 0 °C. Rapid polymerization occured immadiatelly after the addition of EDSP and the viscosity of the solution increased gradually during the polymerization process. After 2 h. the solution was poured into acetone-water mixture. The resulting polymer was filtered and washed with water and alchol and dried under vacuum at room temperature. Under similar conditions other polymers containing various adipoyl segments were obtained.

ANALYSIS

IR spectra were taken by Jasco FT-IR 5300 using KBr discs. ^{1}H-NMR measurements were performed with Bruker SD1823 in DMSO-d_6 solution using tetramethylsilane served as internal standart. Melting points and decomposition temperature were determined on a Perkin-Elmer DSC-1B calorimeter under nitrogen at a 8 °C/min heating rate. Thermal gravimetric analysis was carried out with a Du Pont Instrument.

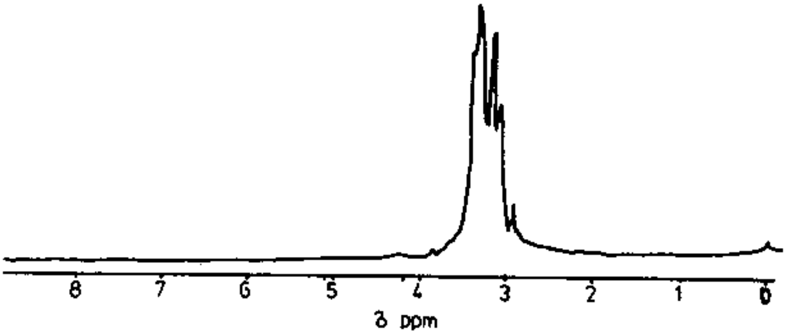


Fig 1. ^{1}H-NMR Spectrum of EDSP.

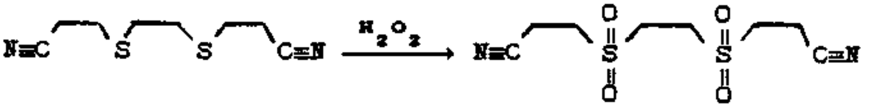
Table 1
Polymerization of EDSP with Trioxane in Sulfuric Acid[a]

EDSP/H_2SO_4	H_2SO_4	[Trioxane]10^4M	[EDSP]10^4M	Yield (%)
1/10	3.78	1.2	3.78	27.81
1/20	7.56	1.2	3.78	31.45
1/30	11.34	1.2	3.78	43.18
1/40	15.12	1.2	3.78	53.91

a: Reaction temperature 0°C, 90 min.

RESULTS AND DISCUSSION

The synthesis of sulfone dinitrile compound, as illustrated in scheme 1, was performed using general sulfonation process [9].



(3)

The structure of EDSP was confirmed by spectroscopic investigation. The IR spectrum contains characteristic C-H and C≡N bands at 2950 cm^{-1},2250 cm^{-1} respectively and 0=S=0 groups 1425, 1175 and 1125 cm^{-1}. The ^{1}H-NMR spectrum recorded in DMSO-d6

Table 2
Polymerization of EDSP and Adipoyldinitrile (AD) with Trioxane in Sulfuric Acid [a]

Code	EDSP+AD/H_2SO_4 (mol ratio)	Trioxane	AD	EDSP	Yield (%)
PAA	1/20	0.7	2.1	-	22.3
PAAS1	1/20	0.7	1.68	0.43	14.87
PAAS2	1/20	0.7	1.05	1.05	11.48
PAAS3	1/20	0.7	0.43	1.68	9.19
PAS	1/20	0.7	-	2.1	5.72

a: Reaction temperature 0°C, 90 min.

evidenced resonance signals of the CH_2 groups between 3-3.5 ppm (Fig.1).

For preparing PASs, a procedure developed earlier for poly(amidethioether) was followed; thereby pure PASs could be obtained in 30-50% yields. The synthesis is a one pot reaction of the dinitrile compound and trioxane in strong acid such as sulphiric acid at low temperature. Typical polymerization reaction for various molar ratios of sulfuric acid are shown in Table 1.

To investigate the effect of partial replacement of EDSP with adipoyldinitrile, polyamide sulfone copolymers (co-PAS) containing 20-80 mol% of EPSP and 80-20 mol% of adipoyldinitrile were synthesized. All of the polymers were obtained in similar yields (Table 2).

PASs and co-PASs obtained were characterized by IR and ^{1}H-NMR spectra. The IR spectra of all polymers showed characreristic IR absorption at 2950 cm^{-1} (aliphatic CH strectching), 3300-3250 cm^{-1} (N-H-stretching), 1650 cm^{-1} (amide I, C=O stretching), 1550 cm^{-1} (amide II, interaction of -NH- bending and C-N stertching of C-N-H) and at 1380 and 1160 cm^{-1} (O=S=O stretching) (Figure 2a). Incorporation of adipoyl segments into PAS does not bring additional bands in the IR spectra of polymers since CH groups are already present in the structure (Figure 2b).

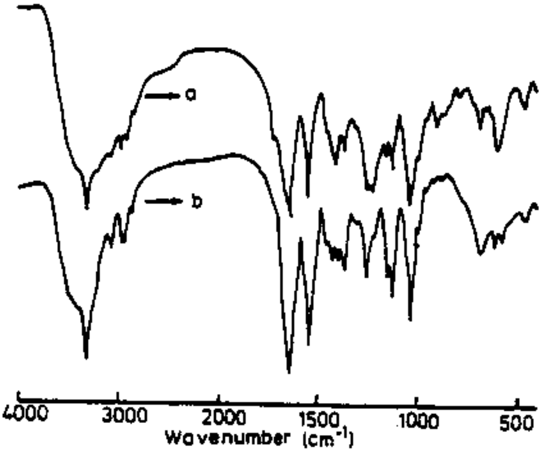


Fig. 2 Infrared spectra of (a) PAS, (b) co-PAS (PAAS2).

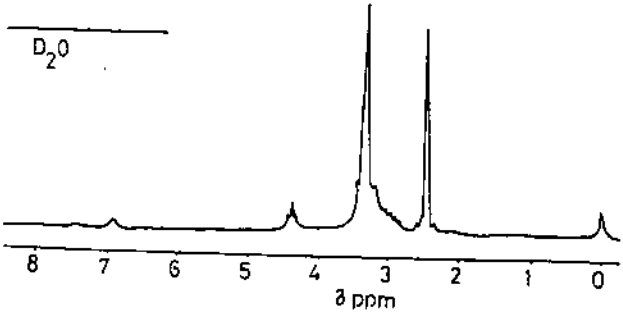


Fig. 3 ^{1}H-NMR Spectrum of co-PAS (PAAS2).

Table 3
Solubilities of copolyamides, obtained from EDSP and AD.

Solvent	PAA	PAAS1	PAAS2	PAAS3	PAS
DMSO	SS	S	S	S	I
DMA	I	I	I	I	I
NMP	I	I	I	I	I
Formic acid	SS	SS	SS	SS	SS
Sulfuric acid	SS	SS	SS	SS	SS
m-Cresol	S	S	S	S	S
THF	I	I	I	I	I
DMF	I	I	I	I	I
NMP/ Pyridine	I	I	I	I	I

SS: Soluble at room temperature S: Soluble on heating
I: Insoluble

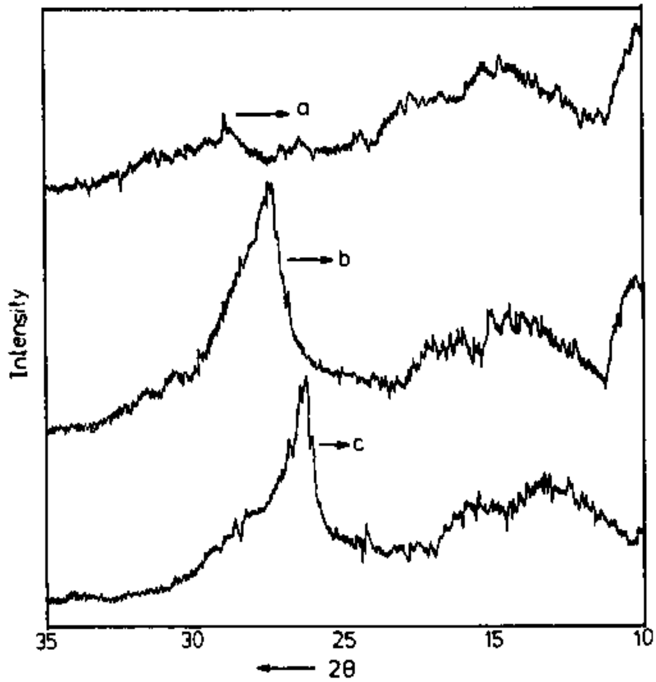


Fig. 4 X-ray diffraction of polyamides (a) PAS.
(b) PAAS3.
(c) PAAS1.

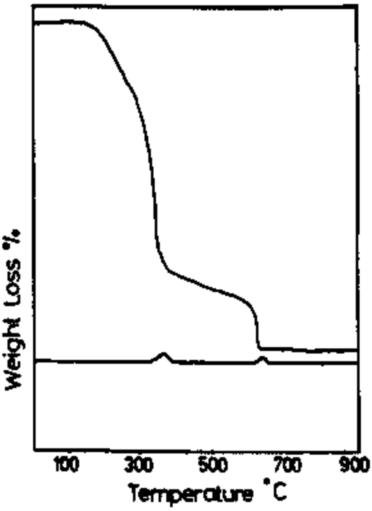


Fig. 5 TG curve of polyamide PAAS2.

^{1}H-NMR spectrum of a typical DMSO soluble co-PAS posseses bands of CH_2 protons at 3.3 ppm range, -NH protons were detected as a weak signal at 7 ppm because of intermolecular exchange and hydrogen bonding [10]. Exchange with D_2O results in the disappearance of this signal at 7 ppm (Fig.3).

PASs are insoluble in all organic solvents. Incorporation of adipoyl segments (co-PAS) improved solubility to some extend (Table 3).

The polyamides possessing adipoyl segments namely PAAS1 and PAAS3, exhibit partial crystalline pattern whereas PAS were found to be amorphous (Fig.4).From this result it can be concluded that adipoyl segments increases the crystallinity of the polyamide.

The thermal stability of PAS's was studied by thermogravimetric analysis (TGA). The polymers began to decompose around 175 °C with a 78.4% weight loss occuring 175-375 °C (Fig.5). Two distinct plateaus observed may be atributted to the decomposition of sulfone and adipoyl segments. It is clear that PASs do not show good thermal stabilities as aromatic polyamidesulfones where rigidity is achived by phenyl groups.

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