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Synthesis and characterization of polymers having –NH–SO–NH–group in the backbone

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SUMMARY

A new monomer 4 has been prepared from the reaction of p-phenylenediamine and excess of thionyl chloride. Reaction of 4 with benzidine in NMP or DMF at elevated temperature resulted a new polymer having —NH—SO—NH—functionality in the backbone. The monomer and the polymer have been characterized by elemental analyses and spectroscopic informations.

INTRODUCTION

The search for new materials for specific applications has received a great deal of attention in the past few years (1-5). One of the promising yet underexploited avenue is the synthesis of polymers having unusual linkages in the polymeric backbone. Monomers bearing two —N=C=O groups have been reported in the literature since a long time and literally hundreds of polyurethanes are made out of them (6). Some of the synthesized polyurethanes have found interesting applications in our daily life. Surprisingly report of the synthesis of compounds bearing two —N=S=O functionalities are extremely rare in literature. Since —N=S=O group is electronically equivalent (isosters) to isocyanate functionality, we thought that reaction of any appropriate nucleophile (Nu^-) to the molecule R--N==S==O should provide a compound of structure 2.

$$\underset{1}{R{-}N{=}S{=}O} \quad + \quad Nu^- \quad \longrightarrow \quad \underset{2}{R{-}NH{-}SO{-}Nu}$$

Thus, in principle, starting with a compound having two sulfinylimine groups and reacting it with a diamine, one would expect a polymer having —NH—SO—NH— group in the polymeric backbone. Due to the unusual combination of heteroatoms in the backbone of the molecule, this type of polymers have a high potential of possessing interesting physical, physicochemical and electrical properties (9). This communications reports our preliminary investigation on the synthesis of a new monomer 4 and its polycondensation reaction with diamine 5 to give the polymer 6. Their characterization procedure is also described.

EXPERIMENTAL

All the chemicals used were purchased from Aldrich Chemical Company. p-phenylenediamine was crystallized from methylene chloride-hexane. Thionyl chloride was purified by distilling over pyridine. Solvents used for the reaction were purified by following the standard procedure (10). All the reactions were carried out under positive nitrogen pressure.

Preparation of 1,4-disulfinylimino benzene 4.

Purified p-phenylenediamine (2.16gm, 0.002mol) was taken in a 100ml two neck round bottom flask which was fitted with a dropping funnel and an water condenser. To it thionyl chloride (50ml) was added slowly while maintaining the temperature of the reaction mixture at 5-10^{o}C. After the addition is complete the reaction mixture was refluxed for 4 hrs and the excess thionyl chloride was removed by rotary evaporator. A yellow solid was obtained which was further crystallized from ether-hexane. The yield of the reaction was 92% and the compound has a M.P. of 112^{o}C. The R_f of the monomer has found to be 0.61 in ethyl acetate - hexane (1:1) solvent system.

The monomer was soluble in most of the organic solvents except n-hexane, cyclohexane and pentane.

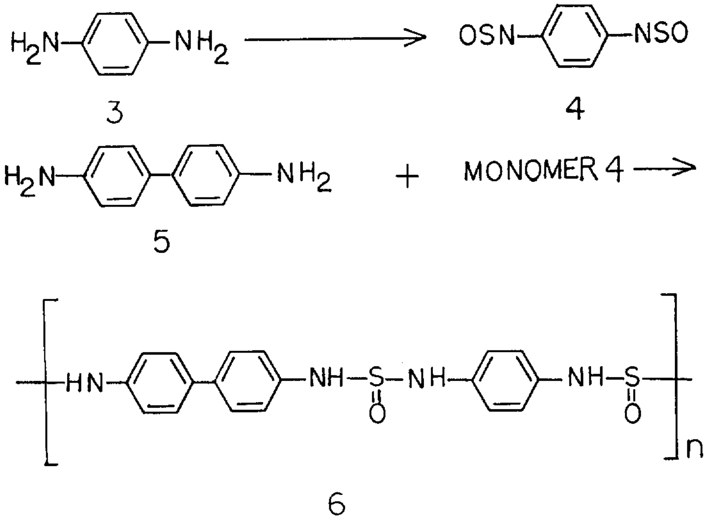
Preparation of polymer 3.

Purified monomer (0.01mol) was taken in DMF or NMP (250ml) solvent. To it a solution of benzidine (0.01mol) in DMF or NMP (100ml) was added slowly over a period of 1/2hr. The reaction vessel was evacuated and purged with dry nitrogen gas. This process was repeated 3 times after which the reaction mixture was heated on an oil bath maintained at 110^{o}C. The color of the reaction mixture turned from yellow to red to black. After 6 hours, the reaction mixture was cooled and was poured into ice water. The precipitated black solid was filtered out. The polymer was further purified by reprecipitation from DMF-ether solvent system. Yield 71%.

The polymer is soluble in DMF, NMP, DMAC, dioxane, HCOOH etc. and insoluble in n-hexane, pentane, cyclohexane and ether.

RESULTS AND DISCUSSIONS

The synthetic procedure adopted to prepare the monomer and the polymer is outlined in scheme 1.



SCHEME-1

The IR of monomer 4 taken in chloroform, shows bands at 1220 cm^{-1} and 1335 cm^{-1} which corresponds to the -N=S=O functionalities. A moderately strong band at 1601 cm^{-1} is assigned for the aromatic group (12).

The ^1H-NMR spectrum of 4, taken in $CDCl_3$ exhibits only one signal at 7.9δ which is assigned to aromatic protons (Figure 1). As expected from the structure of 4, the magnetic equivalency of all four aromatic protons are established from ^{1}H-NMR. The absence of signals due to protons of the primary aromatic amino group is clearly indicative of the structure of compound 4. ^{13}C-NMR (proton noise decoupled) shows two signals at 127 and 148δ. The two quaternary carbons attached to the electron withdrawing -N==S==O group came at 148δ whereas the other four carbons exhibit signal at 127δ. Elemental analyses also supports the structure. The monomer has been found to be very sensitive to light and moisture but is stable under nitrogen and low temperature over a long period of time. Attempts to purify the monomer by Flash column chromatography were unsuccessful. Crystallization, however,could provide analytically pure sample.

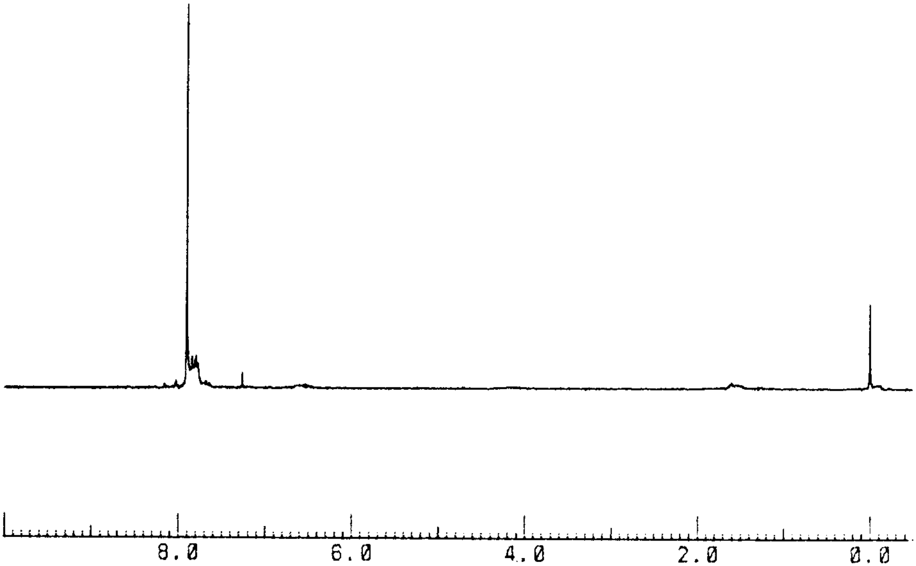


FIGURE 1 : ^{1}H NMR OF MONOMER 4

The structure of the polymer has been supported by elemental analyses. The IR spectrum of the polymer taken in nujol mull shows two bands at 1365 and 1230 cm^{-1} which are due to asymmetric and symmetric stretching vibrations of O=S functionality. A rather broad band at 3350 cm^{-1} arises due to the presence of -NH-stretching vibration.

The inherent viscosity of the polymer was taken in NMP and was found to be 0.09 dl/g. This indicates that the synthesized compound is a low molecular weight polymer. We think that the dimerization of monomer 4 (in analogy with isocyanate systems) could probably be a competitive reaction (12) which interferes in the polycondensation process , thus lowering the molecular weight of the polymer.

A preliminary study reveals that the polymer is not thermally very stable at high temperatures in air. The results of isothermal aging at 200°C in air and in nitrogen is provided in Table 1. After 10 hours, a weight loss of 12.7% and 7.4% in air and in nitrogen respectively were observed. The nonbonding repulsive interactions of the loan pairs of nitrogen and sulphur makes the N-S bond unstable. This instability of the N-S bond probably facilitates the oxidative decomposition process more in air than in nitrogen.

Table 1.

Isothermal Aging of the polymer 4 at 200°C.

Aging Time, hr	1	2	4	8	12
Weight loss in air, %	2.6	3.1	6.4	9.5	12.7
Weight loss in nitrogen, %	0.7	1.9	2.6	4.9	7.4

CONCLUSIONS

Synthesis of a new monomer is described which on polycondensation reaction with a diamine yields a new type of polymer having -NH-SO-NH- functionality in the polymeric backbone. The possibilities of utilizing this class of monomer to get different types of new polymers is very high. Investigations on the general applicability of the reaction, studies on the reaction mechanism and the synthesis of other new polymers are in progress. The detailed report will be published in future.

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