

OPTIMIZATION OF THE REACTION OF PHTHALIC ANHYDRIDE WITH P₄S₁₀

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Abstract

Polyisothianaphthene can be synthesized by reaction of phthalic anhydride with P₄S₁₀. To make the reaction economically, as well as ecologically acceptable it was necessary to increase the yield of PITN. Therefore, the influence of reaction parameters such as reaction time, quantity of xylene and catalyst were investigated. Changing these parameters a yield of 85% was achieved what is almost double the value achieved in previous experiments.

Introduction

In the field of conjugated electroconductive polymers there is a special group of so-called low band gap polymers. The first polymer of this group was poly(isothianaphthene) (PITN) which have drawn great attention by its much higher conductivity in the neutral state than other conjugated polymers, its high contrast and reversible color change from blue in the neutral state to greenish-yellow in the doped state as well as nonlinear optical properties. [1,2,3] Later other low band gap polymers were synthesized but PITN remains the most studied. [4,5,6]

Several synthetic pathways to PITN are described in literature. It can be prepared by electrochemical polymerization of isothianaphthene (ITN) [1], or disilyl derivatives of

ITN [7] to obtain films deposited on the electrode surface. Chemically it can be synthesized by oxidation of dihydroisothianaphthene with FeCl_3 [4], N-chlorosuccinimide [8] or O_2 [9] to obtain powdery products.

PITN can also be prepared via a precursor route by dehydrogenation of poly(dihydroisothianaphthene) (PDHITN) with dehydrogenation agents such as SOCl_2 [10] or tert-butyl hypochlorite. [11] This method is especially interesting because it leads to a stable PITN solution, so that the films can be prepared by casting.

Recently a novel synthetic route to PITN based on the reaction of phthalic anhydride, phthalic acid or phthalide with phosphorus pentasulphide was discovered. [12,13] The major advantages of this route are availability, chemical stability and low cost of the starting materials as well as the synthetic simplicity of the reaction. Using phthalide as the starting material in xylene the yield of PITN was 80-90 %, while with using phthalic anhydride the yield was only 45%. Xylene appears to be the best solvent for this reaction. When using solvents with lower boiling points like toluene or THF, only thio- compounds and traces of PITN were formed. Using solvents with higher boiling points, like mesitylene or dichlorobenzene, increased the yield but changed the structure of PITN due to the side reactions and chain defects. As a consequence of defects in structure the conductivity of PITN was lower.

Since phthalic anhydride is much cheaper than phthalide we decided to reexamine this reaction and find the optimal conditions for the synthesis of PITN making it more profitable from the financial as well as ecological point of view.

Experimental

All syntheses were performed in a nitrogen atmosphere. Commercially available products were used without further purification.

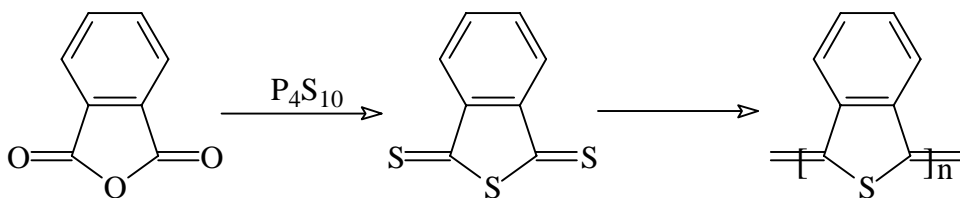
A mixture of phthalic anhydride and P_4S_{10} in xylene was heated to reflux and stirred with a magnetic stirrer. The reactant ratio, quantity of xylene, catalyst concentration and time of reaction were varied as described below. The reaction was stopped by cooling to room temperature. The suspension was filtered and the solid dispersed in 50 ml of

methanol and heated to reflux for one hour. After filtration the black solid was transferred to a Soxhlet extractor and continuously extracted with methanol, THF and CHCl_3 . Each extraction was carried out for 20 hours. The products were dried in vacuum at 80°C .

Results and discussion

The influence of the ratio of reactants

Mechanistic studies of PITN formation from phthalic anhydride have pointed out that trithiophthalic anhydride might be the essential intermediate in the synthesis of PITN, although its isolation was not possible due to its high reactivity. Experiments showed that once the trithiophthalic anhydride is formed the thionating reagent is not a necessity in the polymerization reaction itself. [13,14]



Scheme 1: Synthesis of PITN from phthalic anhydride and P_4S_{10} .

Therefore, theoretically 0.3 mol P_4S_{10} is needed for one mol of phthalic anhydride. All previous research was done with a large excess of P_4S_{10} (0.6-0.7 mol P_4S_{10}).

Using the same reaction conditions as in literature [12] (reactant ratio 1:0.7 mol; 6.2g (0.042 mol) phthalic anhydride, 13.3 g (0.03 mol) P_4S_{10} , 50 ml of xylene, 20 h reaction time) the yield of PITN was 44%. Lowering the amount of P_4S_{10} to 6.2g (0.014 mol) (reactant ratio 1:0.32), the yield dropped to 42%. All the other reactions were made with this reactant ratio since a 2% decrease in PITN yield was acceptable in light of the significant reduction in P_4S_{10} use. In addition, these results confirm the observation that a thionating reagent is not a necessity for the polymerization itself.

The influence of the reaction time

The reaction of phthalic anhydride with P_4S_{10} is slow and after 3 h no PITN was isolated. The product was a mixture of unreacted phthalic anhydride, thiophthalic anhydride, dithiophthalic anhydride, and their dimers. Prolonging the reaction time to 17 and 20 h increased the yield to 40 and 45% respectively. [13]

According to the result above the reactant ratio 1:0.32 was used and the reaction time was varied from 20 to 48 hours. The yield of PITN changed almost linearly with time and yields up to 75% were achieved. The results are shown in Table 1.

Table 1: Yield of PITN in dependence on the reaction time.

Reaction time (h)	Yield of PITN (%)
20	42
30	53
40	66
48	75

The influence of the quantity of xylene

Phthalic anhydride and P_4S_{10} are only partially soluble in xylene. The reaction seems to be heterogenous and the role of xylene is mostly to insure the mixing of reagents and to dissipate the heat that develops during the reaction. Nevertheless, lowering the quantity of xylene from 50 to 40 ml increased the yield of PITN from 42% to 55%. This can be explained by the increase of the contact area between particles of phthalic anhydride, PITN and P_4S_{10} . In the second experiment the reaction time was prolonged to 48 hours. The yield of PITN was 80%, which is only 5% higher compared to the reaction with 50 ml of xylene. Further lowering of xylene quantity was not possible because good stirring could not be assured.

Catalysis of the reaction with p-toluenesulfonic acid

A mechanism for the formation of PITN from phthalic anhydride and P_4S_{10} , based on a sequence of substitution (thionation), isomerization, and polymerization reactions has already been proposed. [13] The first step is a substitution reaction by which a carbonyl is converted to a thiocarbonyl group. The product readily isomerizes to the more stable thiophthalic anhydride, which is thionated to yield dithiophthalic anhydride. This dimerizes to the dithio- dimer or reacts with P_4S_{10} to trithiophthalic anhydride. According to the proposed mechanism, the rate of reaction could be increased by protonating C=O groups. To achieve this *p*-toluenesulfonic acid (*p*-TSA) was chosen as a protonating agent because it is also a well known dopant for some conductive polymers. Through its use we wished to increase the yield as well as dope PITN in one step. In fact, adding 0.06g *p*-TSA (1 wt.% vs. phthalic anhydride) to the reaction mixture increased the yield of PITN to 51%. Further increase of *p*-TSA up to 10% gave a yield of PITN of 52-58%, but the results were scattered and no correlations were found between *p*-TSA concentration and yield of PITN. Scattering can be explained by different granulation of phthalic anhydride, although the yield was reproducible if no or 1% of *p*-TSA was used. From the relatively low increase in yield when 2-10% *p*-TSA was added, compared to 1%, we can assume that the *p*-TSA catalysed only the first reaction and had no influence on the next steps. Since the conductivity of this PITN was even slightly lower (but still in the range of 10^{-1} - 10^{-2} S/cm) we believe that adding 1% of *p*-TSA is an optimum value.

Final optimization of PITN synthesis.

On the basis of these results the final experiment was made in which 6.2g phthalic anhydride, 0.06g p-TSA and 6.2 g P₄S₁₀ in 40 ml xylene were used and the time of reaction was 48 hours. The yield of PITN was 85%, which is almost double the value from the previous experiments.

Conclusion

The reaction of phthalic anhydride with P₄S₁₀ is relatively slow and high yields can only be achieved if long reaction time is used. A reduction of the quantity of xylene used increased the yield but under the experimental conditions 40 ml was the lower limit. Using a mechanical stirrer, a lower quantity of xylene could probably be used. The role of p-TSA is not clearly understood but it is evident that it acts as a catalyst.

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References

- [1] F. Wudl, M. Kobayashi, A. J. Heeger, *J. Org. Chem.*, **1984**, *49*, 3382-3384.
- [2] M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl, A. J. Heeger, *J. Chem. Phys.*, **1985**, *82*, 5717-5723.
- [3] M. Onoda, S. Morita, H. Nakayama, K. Yoshino, *JPN. J. Appl. Phys.*, **1993**, *32*, 3534-3539.
- [4] M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng, W. J. Pomerantz, *Synth. Met.*, **1993**, *55-57*, 960-965.
- [5] M. Hanack, K.-M. Mangold, U. Röhrig, C. M.-Mössmer, *Synth. Met.* **1993**, *60*, 199-210.
- [6] J. P. Ferraris, T. L. Lambert, *J. Chem. Soc. Chem. Commun.* **1991**, *11*, 752-754.
- [7] M. Lapkowski, R. Kiebooms, J. Gelan, D. Vanderzande, A. Pron, T. P. Nguyen, G. Louarn, S. Lefrant, *J. Mater. Chem.* **1997**, *7*, 873-876.

- [8] I. Hoogmartens, D. Vanderzande, H. Martens, J. Gelan, *Synth. Met.* 1992, 47, 367-371.
- [9] K-Y. Jen, R. Elsenbaumer, *Synth. Met.*, **1986**, 16, 379-380.
- [10] T. L. Rose, M. C. Liberto, *Synth. Met.* **1989**, 31, 395-398.
- [11] S. A. Chen, C. C. Lee, *Synth. Met.* **1995**, 75, 187-189.
- [12] R. Van Asselt, I. Hoogmartens, D. Vanderzande, J. Gelan, P. E. Froehling, M. Aussems, O. Aagaard, R. Schellekens, *Synth. Met.*, **1995**, 74, 65-70.
- [13] R. Van Asselt, D. Vanderzande, J. Gelan, P. E. Froehling, O. Aagaard, *J. of Polym. Sci. Part A: Polym. Chem.*, **1996**, 34, 1553-1560.
- [14] H. Paulussen, B. Ottenbourgs, D. Vanderzande, P. Adriaensens, J. Gelan, *Polymer*, **1997**, 38, 5221-5225.

Povzetek

Reakcija med ftalanhidridom in P_4S_{10} vodi do nastanka poliizotianaftena. Da pa bi bila sinteza tako ekonomsko, kot tudi ekološko sprejemljiva, je bilo potrebno povečati izkoristek reakcije. S spreminjanjem časa reakcije, količine ksilena in dodatkom para toluensulfonske kisline kot katalizatorja, smo uspeli izkoristek reakcije povečati na 85%, kar je skoraj dvakrat toliko kot v prejšnjih raziskavah.