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On the Thermal Copolymerization of Styrene with Acrylonitrile

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ABSTRACT: The spontaneous thermal copolymerization of styrene (St) with acrylonitrile (AN) was studied at 100 and 125 °C. Control experiments showed that AN alone does not spontaneously homopolymerize at these temperatures. Dilution with propionitrile, an inert model for AN, showed that, at a 1/4 St/AN feed ratio, the initiating radicals are generated by reaction of St with AN. For a 1/1 feed ratio at 100 °C the copolymerizations proceeded faster than the homopolymerization of St, while a monomer feed of 1/4 St/AN led to the fastest rates. The inherent viscosity was constant with time during the run. Maximum rates were observed for a 40/60 St/AN monomer feed ratio, both in bulk and in propionitrile. The yield of small molecules was very low, reaching a maximum of ~3%. The small molecules consisted mostly of $StAN_2$ trimers, with minor contributions of the St_2AN trimer and StAN–cyclobutane adduct. The latter two were not observed in the 1/6 St/AN run. These results lead us to conclude that a Mayo-type mechanism is in effect for this initiation. The results are compared to the previously studied photochemical polymerization of St and AN.

Introduction

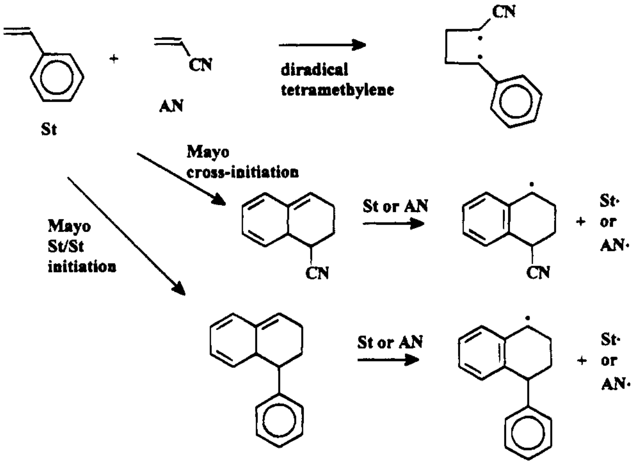
In earlier work we have explored the initiation mechanism for the "charge-transfer copolymerization" and proposed a bond-forming initiation process.[1,2] In this mechanism an electron-rich and an electron-poor monomer combine, often via the charge-transfer (CT) complex, to form a bond at the β (tail) positions resulting in an initiating tetramethylene diradical (or zwitterion). This mechanism was proved kinetically for the *p*-methoxystyrene/dimethyl cyanofumarate monomer pair.[3] The accompanying small molecules, such as cyclobutanes, can provide clues to the nature of the initiating species.

Our work originally utilized powerful acceptor and donor monomers in order to provide rapid spontaneous reactions at room temperature. However, our mechanism should also apply to less polar, more common monomers with the proviso that higher temperatures would be needed to bring about reaction. We have recently studied the reactions that occur upon heating 2,3-dimethyl-1,3-butadiene and acrylonitrile. Spontaneous copolymerization competed with the concerted cycloaddition, and the polymerization results were interpreted in terms of bond-forming initiation.[4] Other dienes reacted similarly.[5]

The copolymerization of styrene (St) with acrylonitrile (AN) seemed to be another good case to test our theory. The bulk reaction is actually carried out thermally by several industrial companies. We have found no kinetics studies published on this important spontaneous reaction, but the initiated copolymerization has been studied in great detail.[6,7] From our point of view, the phenyl group of St is a moderate donor and the single cyano group of AN makes AN a moderate acceptor olefin. St and AN do form a weak CT complex.[6]

During the past four decades two theories for the generation of initiating diracidals have been discussed in great detail. The initiation of a diradical tetramethylene was originally proposed by Flory[8] and anticipated the mechanism we have postulated for the spontaneous polymerization observed for the monomer pairs with great electron disparity.[2] Mayo proposed a different mechanism in which an initial Diels–Alder reaction between two styrene molecules or between styrene and the comonomer led to a 1,2,3,8a-tetrahydronaphthalene derivative.[9] Concerted cycloaddition was followed by H-transfer from the doubly allylic hydrogen on the bridgehead position to another monomer to form two initiating monoradicals. The Mayo mechanism has been generally accepted for the self-initiation of styrene.[10] The two mechanisms are depicted in Scheme 1.

Scheme 1. Possible Initiation Mechanisms



A complicating feature of the study of the spontaneous copolymerization of St and AN is the thermal polymerization of St by itself. Conditions must be found where this can be neglected.

The structure of small molecules accompanying polymer can provide information bearing on the initiation mechanism.[1,2] Detecting the StAN–cyclobutane adduct would be powerful evidence for initiation by a diradical tetramethylene; however, this compound has not yet been reported in this reaction.[11] Schlapkohl and Kirchner reported on the structure of the trimers formed in the spontaneous reactions of St and AN.[12] Recently, Priddy and co-workers reinvestigated the structure of these trimers in more detail.[11] These adducts are composed of two main families, namely, St_2AN adducts composed of two St units and one AN unit, and $StAN_2$

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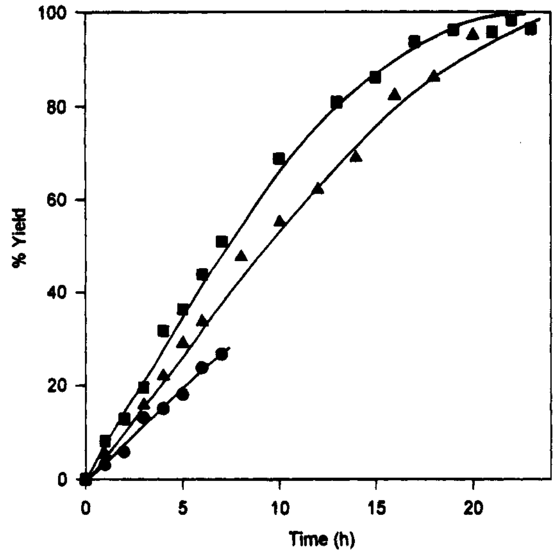


Figure 1. Time–conversion curves for spontaneous polymerizations at 100 °C in bulk: Styrene (●); St/AN 1/1 (▲); St/AN 1/4 (■).

adducts of one St unit and two AN units. Schellenberg and Wigand gave a long list of molecules formed in St/AN copolymerization but only in terms of composition.[13] They did note a St_1AN_1 component and assigned the cyanotetralin structure without structural proof.

The St/AN system possesses another attractive feature. We had earlier studied this system photochemically.[14] Our results were interpreted in terms of an excited styrene molecule reacting with either St or AN to form the respective diradicals ·StSt· and ·StAN·. Accordingly, a study of the thermal reaction will give us a unique opportunity to compare a thermal spontaneous copolymerization with the same combination initiated photochemically. Clearly if the same intermediates are postulated in the two processes, they must give rise to the same product mixtures.

Results

The reaction of St and AN was investigated in bulk and in propionitrile (PN) at 100 or at 125 °C. PN was also used as a nonpolymerizable model molecule for AN. The polymeric products were isolated by precipitation and filtration, and the percent conversion was determined. The solvent was removed from the filtrate, the residue was taken up in ether, and the soluble fraction was analyzed for possible small-molecule adducts. Reproducible data were obtained.

Polymerization Data. AN heated alone or in PN does not polymerize at 100 °C. As is known from the literature, St in bulk does polymerize at 100 °C.[10] For reference the St homopolymer yield at 100 °C was measured as a function of time in our experimental conditions (Figure 1). Dilution of St with PN reduced its homopolymerization rate, as shown in Figure 2 for both 100 and 125 °C. At 100 °C a dilution of more than 4:1 PN versus St lowered the yield to less than 1% after 2 h, while at 125 °C a dilution of more than 6:1 St was needed. Accordingly, free radical (co)polymerization caused by St–St reaction can be eliminated by dilution with PN, or presumably with AN. Any copolymerization occurring beyond these dilutions must be ascribed to a St–AN reaction.

The spontaneous copolymerization of St and AN was investigated at 100 °C at a molar feed ratio of 1:1 and at 1:4, and the results are shown in Figure 1. The copolymerization proceeded faster than the spontaneous homopolymerization of St at this temperature, and the run with excess AN (ratio 1/4) was the fastest. The data for this latter run are listed in Table 1.

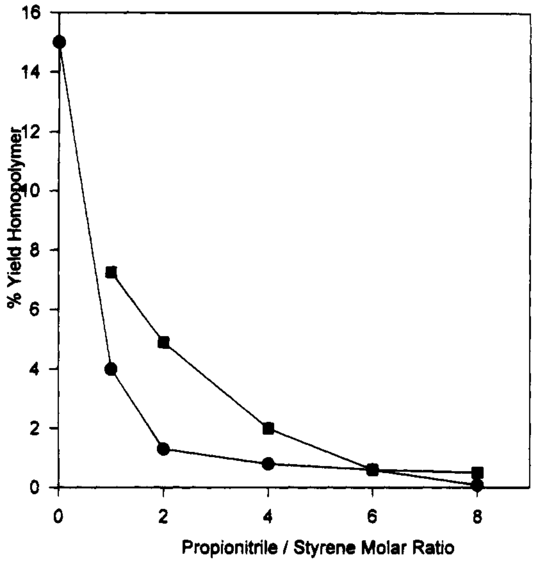


Figure 2. Spontaneous styrene polymerization in propionitrile at 100 (●) and 125 °C (■) (time 2 h).

Table 1. Spontaneous Copolymerization of St and AN at 100 °C (St/AN 1/4)

time (h)	copolymer[a] (wt % yield)	η_{inh}[b] (dL/g)	oligomers and small molecules[c] (wt % yield)	small molecules[d] (wt % yield)
1.0	8.1	1.88	0.01	0.01
2.0	12.8	3.44	0.04	0.01
3.0	19.5	3.38		
4.0	31.6	3.14	0.05	0.05
5.0	36.3	3.39		
6.0	43.7	3.16		
7.0	50.7	2.94	0.05	0.01
10.0	68.8		0.13	0.07
13.0	80.9			
15.0	86.1		0.20	0.02
17.0	93.7			
19.0	96.1		0.17	0.06
21.0	95.7		0.69	0.08
22.0	98.2		2.06	0.45
23.0	96.4		2.94	0.87

[a] Weight percent of fraction precipitated in methanol. [b] Inherent viscosity measured in THF at 30 °C; concentration 0.1 g/dL. [c] Weight percent of fraction precipitated in ether. [d] Weight percent of remaining ether-soluble fraction.

The inherent viscosities of the copolymers produced in bulk were constant at ~2.1 dL/g for the 1/1 St/AN run and at ~3 dL/g for the 1/4 St/AN run. This is remarkable because the copolymer composition is changing during the run.

The spontaneous copolymerization of St and AN was also briefly investigated at 125 °C in bulk. At this temperature a St/AN ratio of 1:6 had to be used to suppress the self-initiation of styrene. The time–conversion curve is shown in Figure 3. The yield vs time plot was linear only up to ~40% conversion and the copolymerization stopped at about 65% conversion, because the styrene had been consumed and no more initiating radicals were being generated.

To further investigate the effect of the molar feed on the rate of the spontaneous copolymerization, the two monomers were heated together either in bulk or with PN as a diluent at 100 °C for 2 h. The results are shown

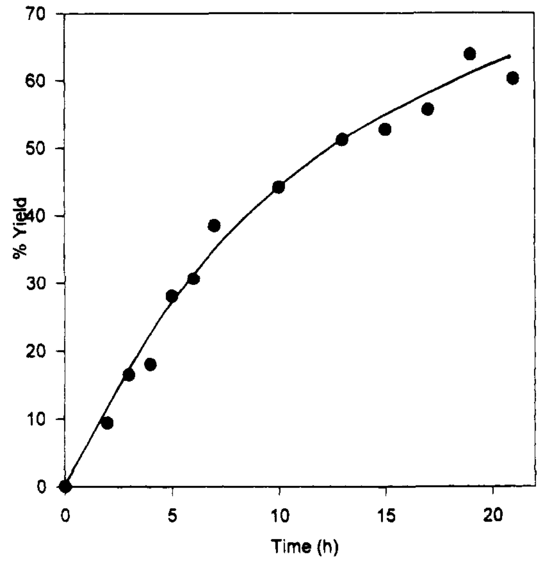


Figure 3. Time–conversion curve for the spontaneous copolymerization at 125 °C in bulk (St/AN 1/6).

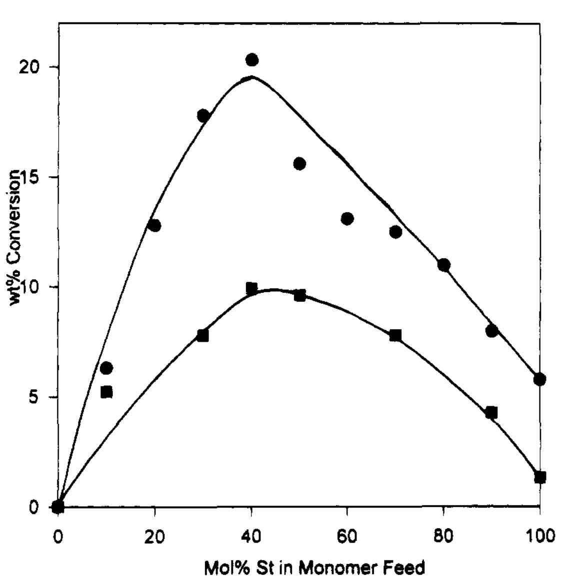


Figure 4. Effect of molar feed ratio on the copolymerization of St and AN (temperature 100 °C): in bulk, time 2 h (●); in dilute conditions, molar ratio of total monomer to propionitrile 1:2, time 4 h (■).

in Figure 4. In each case the highest yield was obtained at ~40 mol % St, ~20% yield in the bulk case and ~10% in the diluted case. The rates were faster in the presence of excess AN, as we had already observed in the time vs conversion curves. This is additional evidence for initiation by a St–AN reaction.

Studies of Small Molecules/Oligomers. After the polymerization was finished and the polymer removed by precipitation, the residual products were taken up in ether and analyzed by GC/MS. The remaining insoluble material was identified as oligomeric. For all runs investigated, the amount of small molecules plus oligomers was very small, reaching a maximum of ~3% (Tables 1 and 2). The yields were not much affected by dilution with PN, by feed ratio, or by temperature.

The ether-soluble fraction, namely, the small-molecule adducts, was analyzed by GC–MS. The results are summarized in Table 3. In the gas chromatograms the first two groups of peaks were identified as $StAN_2$ adducts. At longer elution times, the peaks belonging to a StAN adduct and the St_2AN adducts were observed. These peaks were identified based on the mass spectra and comparison with data from our investigation of the photochemical initiation of the St–AN system[14] and literature data.[11,12]

Table 2. Effect of Feed Ratio on the Spontaneous Copolymerization of St and AN at 100 °C (time 2 h)

monomer feed ratio (mol % St in feed)	copolymer[a] (wt % yield)	oligomers and small molecules[b] (wt % yield)	small molecules[c] (wt % yield)
0	0		
10	6.3		
20	12.8	0.04	0.03
30	17.8	0.04	0.03
40	20.3	0.17	0.14
50	15.6	0.22	0.07
60	13.1	0.27	0.18
70	12.5		
80	11.0	0.43	0.21
90	7.9	1.03	0.30
100	5.8		

[a] Weight percent of fraction precipitated in methanol. [b] Weight percent of fraction precipitated in ether. [c] Weight percent of remaining ether-soluble fraction.

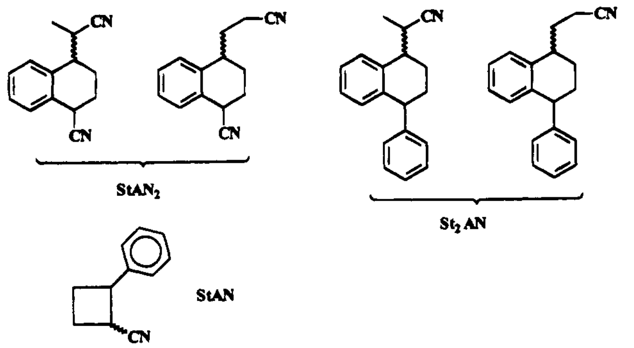
Table 3. Product Distribution for the Small Molecules from GC/MS Analysis

monomer feed comp and reaction temp	$StAN_2$ adducts (GC %)	St_2AN adducts (GC %)	StAN–cyclobutane adduct (GC %)
St/AN 1/1, 100 °C, 2 h	85	2	2
St/AN 1/1, 100 °C, 4 h	63	6	10
St/AN 1/4, 100 °C, 24 h	72	9	0
St/AN 1/6, 125 °C, 24 h	90	0	0
St/AN/PN 2/1/3, 125 °C, 48 h	91	2	7

The structure of the $StAN_2$ adducts had been studied in great detail by Priddy and co-workers.[11] The loss of AN followed by the loss of HCN leads to the base peak at *m/e* 129, which corresponds to the tetralin cation. The data we obtained for the $StAN_2$ adducts are in agreement with those of Priddy and we fully concur with his structure assignment.

The mass spectral fragmentation pattern for the St_2AN adducts lead us to propose a different structure from the structure proposed in the literature for these trimers.[11,12] The spectrum indicates initial loss of acrylonitrile (M = 207), very similar to the fragmentation pattern for the $StAN_2$ adducts. This was followed by a loss of benzene, giving a 90% peak at *m/e* 129, which is the tetralin cation. The base peak is the benzyl cation (M = 91). The previously proposed 1-benzyl-4-cyano-1,2,3,4-tetrahydro-α-methylnaphthalene structure does not lead to the tetralin cation. The proposed St_2AN structure would result from initial Diels–Alder reaction of two styrene molecules, in contrast to the previously proposed Diels–Alder reaction of St and AN. The possible mechanisms for the addition of the third monomer have been described in detail by Priddy and co-workers.[11]

The fragmentation pattern of the StAN adduct is in sharp contrast to the pattern observed for the trimers: the loss of ethylene can be observed and the base peak is at *m/e* 105, which corresponds to the styryl cation. This peak at *m/e* 105 is not observed in the mass spectra of the $StAN_2$ adducts and is a minor peak in the St_2AN adducts. The proposed cyclobutane structure of the 1:1 adduct of St and AN is based on the mass spectra previously obtained in this laboratory from photochemi-



cal addition reactions.[14] The fragmentation with loss of ethylene provides powerful evidence for the cyclobutane structure.

The approximate amounts of each kind of adduct, namely, $StAN_2$, St_2AN, and StAN, were calculated from the gas chromatograms generated in the GC/MS spectroscopy. The results are summarized in Table 3. The majority of adducts belongs to the $StAN_2$ family, while the St_2AN adducts are formed in small amounts but, surprisingly, are still present at a 1/4 monomer feed ratio. The cyclobutane adducts, however, are only observed when the feed ratio is approximately 1/1. The remaining small molecules were unidentified higher molecular weight adducts.

Attempts were made to increase the small-molecule yield by inhibiting the polymerization. Two different inhibitors were tried: 2,2,6,6-tetramethyl-1-piperidinyloxy free radical TEMPO and 4,4′-thiobis(2-*tert*-butyl-6-methylphenol), but neither one succeeded in raising the yield of small molecules.

Discussion

Styrene reacts with acrylonitrile thermally and spontaneously at 100 and at 125 °C. The reactions are readily reproducible. The polymerization proceeds faster when more AN is present in the monomer feed. Copolymer is formed in yields up to ~97%, while small molecules/oligomers form in up to ~3% yield.

The known thermal polymerization undergone by styrene is not responsible for these copolymerizations. Styrene was diluted with propionitrile (PN), an inert model for acrylonitrile, until it no longer homopolymerized. Nevertheless, when acrylonitrile is used as the "diluent" in the same molar ratio, ready copolymerization with acrylonitrile occurred. As acrylonitrile does not spontaneously homopolymerize under these conditions, this is strong evidence for initiation by a reaction of styrene with acrylonitrile.

Further evidence for such an initiation reaction comes from studying the dependence of copolymer yield on the feed ratio. Whether in bulk or diluted with PN, a maximum in copolymer yield occurs at ~40 mol % St. The small discrepancy from equimolar may be attributed to preferential propagation reactivity of the monomers.

We are of course not excluding a contribution of the styrene self-initiation at the equimolar monomer feed ratios, but our results indicate that the St/AN reactions are more efficient. The initiation rates cannot be deduced from this initial study as the propagation rates depend on the monomer feed and, in addition, the copolymerization parameters are temperature dependent.

As mentioned in the Introduction and shown in Scheme 1, two initiation mechanisms are possible, namely, formation of a tetramethylene diradical or a Mayo-type mechanism. The small molecules isolated from the copolymerizations have been analyzed. The main portion of the small molecules was the $StAN_2$ fraction, while the St_2AN and the StAN adducts were minor products. At the higher molar feed ratios, namely, St/AN 1/4 and 1/6, no cyclobutane adducts were detected. A 1/6 St/AN monomer feed excluded the St_2-AN adducts, as would be expected; however, these St_2-AN adducts were still present at the 1/4 feed ratio. Surprisingly, no styrene dimers were detected, even though they may be present in trace amounts. This information on the structure and composition of the small molecules leads us to propose that the initiation mechanism for this spontaneous copolymerization follows the Mayo mechanism, namely, initial Diels–Alder cycloaddition followed by hydrogen transfer to a monomer molecule generating two monoradicals.

It is of interest to compare the thermal spontaneous copolymerization between St and AN with the photochemical reaction studied earlier in the laboratory.[14] There are several differences between the two polymerization modes. The photochemical polymerization proceeded at room temperature, but rather slowly, while higher temperatures were required for the thermal polymerization. In the photochemical polymerization, the yield of copolymer and small molecules was dependent on the monomer concentration, with the small molecules dominating at the lower monomer concentrations, while for the thermal polymerization the copolymerization was always dominant, even when propionitrile was used as a diluent. The main difference between the two polymerization modes though is the composition of the small-molecule fraction: in the photochemical runs only StAN and St_2 adducts were identified, with the majority being cyclobutanes, while in the thermal runs the $StAN_2$ trimers, formed by an initial Diels–Alder cycloaddition, dominated. Only minor amounts of St_2AN trimers and StAN–cyclobutane were detected. No Mayo-type trimers were detected in the photochemical runs.

The postulated mechanism in the photochemical polymerizations involved selective excitation of St, which acted as a diradical and added to either St or AN. We had concluded that the ·StSt· diradical preferred to cyclize while the ·StAN· preferred to initiate. In contrast, we have to postulate a Mayo-type mechanism for the thermal polymerization. We have found clear evidence for cross-initiation for these copolymerizations. The cross-initiation from reaction of St and AN is faster than the St/St reaction as would be expected from the influence of the polarity on the initial Diels–Alder reaction. A diradical tetramethylene as initiator for this system can only play a minor role.

Experimental Section

Methods. Elemental analyses were obtained from Desert Analytics, Tucson, AZ. The inherent viscosities were measured at 30 °C in chloroform in an Ostwald viscometer.

Reactants. Acrylonitrile (AN) and propionitrile (PN), purchased from Aldrich, were purified by distillation over calcium hydride. Styrene (St) was purified by passing over a column of aluminum oxide to remove inhibitor.

Polymerization Procedures. The thermal copolymerizations of acrylonitrile and styrene were carried out in a Pyrex tube equipped with a Teflon valve. Before reaction the tube containing the reaction mixture (acrylonitrile, styrene, and sometimes also containing propionitrile and TEMPO) was put in a dry ice bath and degassed under vacuum three times. The copolymerizations were run in an oil bath at controlled temperature for the time needed.

After polymerization, methylene chloride was added and the tube shaken until the copolymer was solubilized. The solution of copolymer in methylene chloride was added dropwise to excess methanol with stirring to precipitate the polymer (co- or homopolymer). The precipitated polymer was filtered off, collected, and dried in vacuum. A small amount of inhibitor was added to the filtrate solution. Methylene chloride, methanol, and remaining monomer were removed using a rotoevaporator and the residue was dried under full vacuum. Ethyl ether was added and oligomers were precipitated, filtered, and weighed. After removal of ethyl ether, the small molecules were weighed and analyzed using a Hewlett-Packard GC/MS system at 70 eV.

GC/MS Data. The temperature profile of the analysis is as follows: 1 min at 70 °C, increase to 300 °C at a rate of 20 °C/min, 5 min at 300 °C. The peaks were identified by comparison with the results described by Priddy.[11] In this experimental setup, two groups of peaks with dilution times of 10.6 and 11.2 min, respectively, were assigned to $StAN_2$ adducts, while the peaks at 12.3 min were St_2AN adducts. The peak at 12.2 min, when it was observed, was assigned to a cyclobutane adduct of St and AN, based on the fragmentation pattern. Typical MS for $StAN_2$: *m/e* 210 (M^+, 13%), 156 (−AN, 20%), 129 (M^+ − AN − HCN, base peak), 115, 102, 89, 77, 63, 51 (minor peaks). Typical MS for St_2AN: *m/e* 261 (M^+, 42%), 207 (−AN, 40%), 206 (35%), 178, 165, 152, 129 (tetralin cation, 90%), 105 (StH^+, 30%), 91 (benzyl cation, base peak), 77, 51, 39. Typical MS for StAN−cyclobutane, determined by comparison with known spectra:[14] *m/e* 155 (M^+, 16%), 120 (−ethylene, 10%), 116, 105 (−AN, base peak), 77, 69, 56, 51 (minor peaks).

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