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Oligomer Formation and the Mechanism of Initiation in the Spontaneous Copolymerization of Styrene and Acrylonitrile

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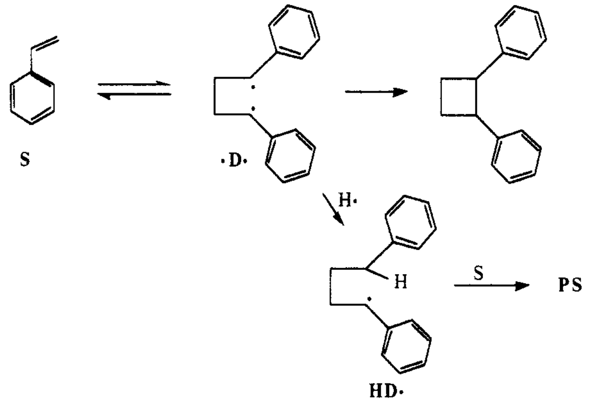
ABSTRACT: The structures and stereochemistry of the trimers, containing two acrylonitrile units and one styrene unit (An_2S), produced during the spontaneous copolymerization of styrene (S) and acrylonitrile (An) were determined using ^1H NMR, ^{13}C NMR, and X-ray crystallography. High-pressure liquid chromatographic (HPLC) conditions are described for the separation of the oligomers. One of the An_2S stereoisomers was obtained as a pure crystalline compound. Its thermochemistry was studied to gain insight into its origin. This information together with the results of other experiments (the effect of acid on SAn polymerization kinetics and the ability to spontaneously copolymerize 2-vinylmesitylene and acrylonitrile) indicates that the "Mayo mechanism" is not responsible for initiation of SAn copolymerization.

Introduction

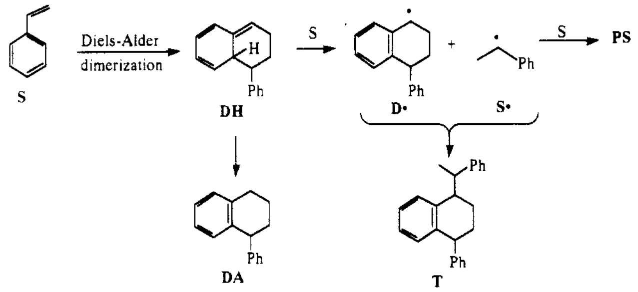
The self-initiated (spontaneous) polymerization and copolymerization of vinyl monomers have challenged researchers for many years. Styrene homopolymerization has been studied in the greatest detail. Two mechanisms have been proposed to explain the formation of initiating radicals. The oldest mechanism was postulated by Flory[1] (Scheme I) over 50 years ago. It involves the formation of a diradical intermediate ($^{\bullet}D^{\bullet}$) en route to a 2 + 2 styrene dimer. The 1,2-diphenylcyclobutane thus formed is the major dimer present in polystyrene. The diradical can also abstract a hydrogen atom, forming a monoradical initiator ($HD^{\bullet}$) which reacts with more styrene (S) to yield polystyrene (PS). More recently, other researchers have gained evidence in support of this mechanism.[2-5]

Scheme I
Flory Mechanism for Spontaneous Styrene Polymerization



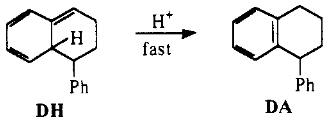
The second mechanism was proposed by Mayo[6] (Scheme II) and involves an α regioselective Diels–Alder dimerization to a reactive triene (DH), which rapidly undergoes hydrogen abstraction [molecular assisted homolysis (MAH)] by another monomer unit to form a radical pair. This radical pair can initiate polymerization, or it can collapse to a trimer (T). The Mayo mechanism has been generally preferred even though critical review[2,3] have pointed out that the mechanism is only partially consistent with the available data. Also, the hypothetical intermediate DH has never been seen. Evidence supporting the Mayo mechanism includes the isolation of DA[7,8] and T[9] from styrene polymerizations and the identification of $D^{\bullet}$ as an end-group in polystyrene using ^1H NMR and UV spectroscopy.[10]

Scheme II
Mayo Mechanism for Spontaneous Styrene Polymerization



Recently the spontaneous polymerization of styrene was studied in the presence of various acid catalysts.[11,12] In an acid environment, the reactive Diels–Alder dimer DH was quickly aromatized to inactive DA (Scheme III). This resulted in decreased rates of initiation and decreased formation of T because DH is the precursor of both. The results further support the Mayo mechanism for the spontaneous polymerization of styrene.

Scheme III
Acid-Catalyzed Aromatization of a Reactive Styrene Dimer



Hall and Padias have studied the spontaneous copolymerization of a number of monomer combinations and have proposed a "bond-forming initiation theory".[13,14] They found that the donor/acceptor nature of comonomer pairs controls the nature of the initiation mechanism. They have categorized most spontaneous copolymerizations as going through either tetramethylene diradical or zwitterionic intermediates depending upon the donor/receptor strength of the monomer pair.

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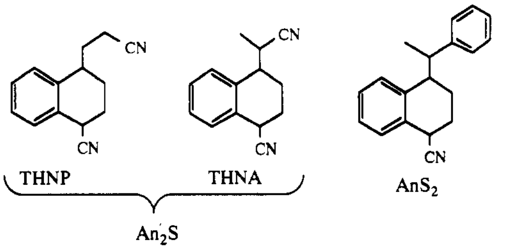


Figure 1. SAn trimer structures previously found in SAn.

Until now, Kirchner and Schlapkohl have been the only researchers to look specifically at the spontaneous polymerization of styrene (S) with acrylonitrile (An).[15] They successfully isolated three trimers using gas chromatography. The structures, but not the stereochemistry, of the trimers were determined (Figure 1) using ^{1}H NMR and mass spectroscopy. Two of the trimers were formed from two An units and one S unit (An$_2$S) and the remaining one from one An unit and two S units (AnS$_2$).

These structures led Kirchner and Schlapkohl to favor the Mayo mechanism for the spontaneous copolymerization of S and An. Their finding of 4-cyano-1,2,3,4-tetrahydro-1-naphthalenepropionitrile (THNP) was surprising since the corresponding all-styrene trimer structure has never been reported. They point out that THNP is likely formed via a concerted Alder-ene reaction between 1-cyanotetralin and An because the radical combination mechanism should favor formation of 4-cyano-1,2,3,4-tetrahydro-α-methyl-1-naphthaleneacetonitrile (THNA) due to the poor stability of the β-cyanoethyl radical.

Clearly, then, the presence of certain trimer structures alone cannot serve to differentiate between the Mayo radical pair mechanism and the Flory diradical mechanism, since the trimers could be formed via concerted mechanisms. However, the Alder-ene and Mayo pathways predict different regiochemistry and stereochemistry for these trimers. In particular, the radical pair closure in the Mayo pathway should produce all four stereoisomers at the newly formed C–C bonds in similar amounts. Conversely, the ene reaction should form the new C–C bonds somewhat stereoselective.[16] Therefore, to see if the trimers constitute evidence for the Mayo radical pair mechanism, their stereochemistry must be determined. Combination of this information with the effects of acid[11,12] on the initiation rate and the ability to copolymerize acrylonitrile with a styrenic monomer (2-vinylmesitylene) incapable of polymerizing by the Mayo mechanism gives insight as to the SAn spontaneous copolymerization initiation mechanism.

Experimental Section

Materials. Camphorsulfonic acid (CSA) and diphenylmethane were obtained from Aldrich Chemical Co. All solvents were obtained from Fisher Scientific and were of HPLC grade. Styrene was produced by The Dow Chemical Co. and contained 3 ppm of *tert*-butylcatechol (TBC). Acrylonitrile (40 ppm of *p*-methoxyphenol) was obtained from Du Pont. 2-Vinylmesitylene (VM) was purchased from Monomer-Polymer and Dajac Laboratories, Inc. The inhibitors were removed by dissolving the VM in methylene chloride and filtering the solution through a column containing neutral alumina AG 7 followed by evaporation of the methylene chloride. TBC (10 ppm) was added to the purified VM to prevent oxidation.

Isolation of SAn Oligomers. SAn copolymerization was carried out by thermal polymerization in a continuous stirred tank reactor.[17] The syrup obtained from the polymerizer contained 55% w/w polymer (25% w/w An units in the polymer). The syrup was continuously pumped into an evacuated (<10 mmHg) tank heated at 240 °C. Molten polymer was pumped from the bottom of the tank. The volatile components were passed through a condenser heated at 100 °C, where the least volatile (mainly trimers) components were condensed to form a syrup.

Solvent Fractionation of the Oligomers. The oligomer syrup was placed in a continuous distillation/extraction apparatus. Isooctane was vaporized, condensed, and passed through a reservoir containing the syrup until the volume of the syrup remained constant. The final volume of the syrup was about 80% of its initial volume. The syrup was analyzed by HPLC, which showed that it contained >95% w/w An$_2$S trimers (Figure 5).

The syrup was then placed in a refrigerator. After 1 week, the crystals which had formed were separated and washed with toluene. The crystals were recrystallized two times from toluene to give white needles (mp = 112 °C). Analysis of the crystals by HPLC showed that they were the last eluting (most polar) An$_2$S trimer.

Gas Chromatographic (GC) Analysis. GC analyses were performed using a Hewlett-Packard 5890A equipped with a flame ionization detector and a 0.25 mm × 30 m (0.25-μm film thickness) DB-17 (100% methylphenylpolysiloxane) capillary column. The oven temperature was controlled at 230 °C for 10 min and then ramped at 5 °C/min to 280 °C.

High-Pressure Liquid Chromatographic (HPLC) Analysis. The oligomer mixture was analyzed by normal-phase liquid chromatography. A CN column and an isooctane/tetrahydrofuran (IO/THF) gradient was found to give good resolution of the oligomers (Figure 4). The conditions were as follows: column, 4.6 mm × 15 cm Spherisorb CN (3 μm); mobile phase, IO/THF at 1 mL/min; gradient, 100% IO → 80/20 v/v IO/THF at 10 min; instrument, Hewlett-Packard 1090M equipped with a diode array detector.

Kinetic Pyrolysis of *cis*-4-Cyano-1,2,3,4-tetrahydro-α(*R*)-methyl-1-naphthaleneacetonitrile. Kinetic pyrolyses were performed by dissolving *cis*-4-cyano-1,2,3,4-tetrahydro-α(*R*)-methyl-1-naphthaleneacetonitrile in diphenylmethane (25/75 w/w) and sealing the mixture in silanized glass tubes (in vacuo). The tubes were then placed in molten salt (40/7/53 w/w/w NaNO$_2$/NaNO$_3$/KNO$_3$) at 265 °C. A tube was removed periodically, and the contents were analyzed by GC. The diphenylmethane served as both a solvent and internal standard. Diphenylmethane was found to be thermally stable under the conditions of the experiment.

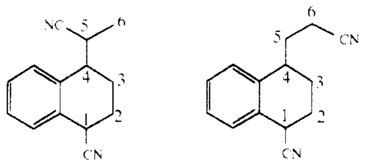
Ampule Polymerizations. Monomers were loaded into glass ampules (7 mm o.d. × 5 mm i.d.), frozen in dry ice, sealed under vacuum (<0.5 mmHg), and placed in a hot oil bath for 1 h at 140 °C. The ampules were removed from the oil bath and allowed to cool to room temperature before being frozen again and opened. A portion of the contents was used to determine conversion by gravimetric analysis. Another portion was poured into methanol to precipitate the polymer. The precipitated polymer was air-dried and subjected to molecular weight analysis using gel permeation chromatography (GPC).

Preparative HPLC Separation of SAn Trimers. Due to the difficulty of isolating pure samples when collected fractions containing THF (peroxide impurities) were evaporated down, an isocratic HPLC method was developed using an 85/15 v/v heptane/methylene chloride mobile phase. The latest eluting peaks showed rather severe tailing. Addition of a little (0.15% w/w) methanol to the mixture eliminated the tailing problem.

The resolution using isocratic conditions was poor. Instead of six An$_2$S trimer peaks, only three peaks were observed. The three peaks were collected from the preparative HPLC. The first cut consisted of the first three peaks in the chromatogram from the analytical column. The second cut was pure and consisted of the fourth An$_2$S trimer peak. The last cut was a mixture of the last two peaks appearing in the chromatogram off the analytical column. The oils that remained after the three cuts evaporated were analyzed by ^{1}H NMR and ^{13}C NMR.

NMR Analyses. Each preparative HPLC oligomer cut was dissolved in deuterochloroform. The 50.3-MHz ^{13}C{^{1}H} NMR spectra were acquired on a Bruker AC200 NMR spectrophotometer operating at a field strength of 4.7 T. When samples composed of a single compound were analyzed, 500 scans were taken. For the multicomponent oligomer cuts, 50 000 scans were necessary to obtain sufficient signal.

Table I
^{13}C NMR Assignments for the Six An_2S Trimers



carbon no.	HPLC peak					
	1	2	3	4	5	6
1	30.32	31.05	32.07	31.19	31.00	30.76
2	25.58	25.02	25.67	24.37	24.26	24.46
3	23.40	21.86	23.63	25.08	24.78	24.06
4	39.06	38.92	39.97	35.76	35.94	40.06
5	29.99	31.39	31.33	32.01	31.96	30.84
6	13.91	13.31	16.41	15.13	15.20	16.26

Table II
Positional and Equivalent Isotropic Thermal Parameters for *cis*-R-THNA, Which Crystallizes in Orthorhombic Space Group $Pna2_1$, with Cell Parameters a = 13.618 (1), b = 9.991 (2), c = 8.701 (2) Å; V = 1183.8 (5) Å^3

atom	x	y	z	B(eq)
C1	0.1255 (2)	0.4528 (3)	0.0056	3.3 (1)
C2	0.1591 (2)	0.5824 (3)	−0.0184 (6)	4.2 (2)
C3	0.2463 (3)	0.6059 (4)	−0.0921 (7)	5.2 (2)
C4	0.3008 (3)	0.4987 (4)	−0.1439 (6)	5.2 (2)
C5	0.2679 (2)	0.3709 (4)	−0.1240 (6)	4.4 (2)
C6	0.1785 (2)	0.3442 (3)	−0.0494 (5)	3.4 (2)
C7	0.1466 (2)	0.2000 (3)	−0.0268 (6)	3.6 (2)
C8	0.1518 (2)	0.1184 (3)	−0.1764 (6)	4.0 (2)
C9	0.1366 (3)	−0.0315 (4)	−0.1523 (7)	5.6 (2)
C10	0.0794 (3)	0.1695 (4)	−0.2872 (7)	4.8 (2)
N11	0.0228 (3)	0.2066 (4)	−0.3720 (6)	7.6 (3)
C12	0.0455 (3)	0.1885 (4)	0.0504 (6)	4.3 (2)
C13	0.0315 (3)	0.2928 (4)	0.1722 (6)	4.7 (2)
C14	0.0333 (2)	0.4322 (4)	0.1008 (6)	3.9 (2)
C15	−0.0555 (2)	0.4537 (4)	0.0082 (6)	4.3 (2)
N16	−0.1245 (2)	0.4662 (4)	−0.0633 (6)	6.3 (2)
H1	0.120 (2)	0.658 (3)	0.021 (5)	5.0
H2	0.271 (2)	0.705 (4)	−0.112 (5)	6.2
H3	0.362 (3)	0.514 (4)	−0.197 (5)	6.0
H4	0.306 (2)	0.295 (3)	−0.156 (5)	5.5
H5	0.195 (2)	0.157 (3)	0.039 (4)	4.2
H6	0.215 (2)	0.135 (4)	−0.219 (4)	4.9
H7	0.183 (3)	−0.060 (4)	−0.065 (5)	6.7
H8	0.145 (3)	−0.072 (5)	−0.243 (5)	6.7
H9	0.068 (3)	−0.052 (4)	−0.114 (5)	6.7
H10	0.038 (2)	0.095 (4)	0.097 (4)	5.3
H11	−0.004 (3)	0.205 (3)	−0.026 (5)	5.3
H12	−0.030 (3)	0.278 (4)	0.221 (5)	5.5
H13	0.093 (3)	0.281 (4)	0.256 (4)	6.0
H14	0.031 (2)	0.502 (3)	0.174 (5)	4.3

In this study only the paraffinic region of the spectrum was used for structural interpretation. To avoid matrix effects upon the chemical shift data, the spectra were recorded using relatively dilute solutions. By doing so, the chemical shift data obtained from the mixtures are independent of the ratio of the components, thus enabling direct comparison of the data.

The carbon multiplicities (i.e., the number of attached protons) were determined using DEPT-135. In this experiment, the methine and methyl carbons have the same phase while methylene carbons possess the opposite phase. Quaternary carbons are not detectable by the DEPT experiment and are thus identified by comparison with the standard $^{13}C\{^1H\}$ NMR spectra.

Spectral assignments were established using spin network correlations obtained from ^1H COSY and $^{13}C\{^1H\}$ heteronuclear correlation (HETCOR) spectra. These assignments are shown in Table I for the six An_2S trimers. The data are reported for the trimer responsible for producing each of the six HPLC peaks shown in Figure 5. These assignments were established through ^1H–^{13}C 2D HETCOR experiments.

X-ray Crystallography. Measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Mo Kα radiation and a 12-kW rotating anode generator. Data were collected at 50 kV and 180 mA at ambient temperature. Data were collected at a maximum scan speed of 16°/min in ω. Weak reflections were rescanned and the counts accumulated to assure good counting statistics. Stationary background was recorded on each side of every reflection. The ratio of peak counting to background counting time was 2:1.

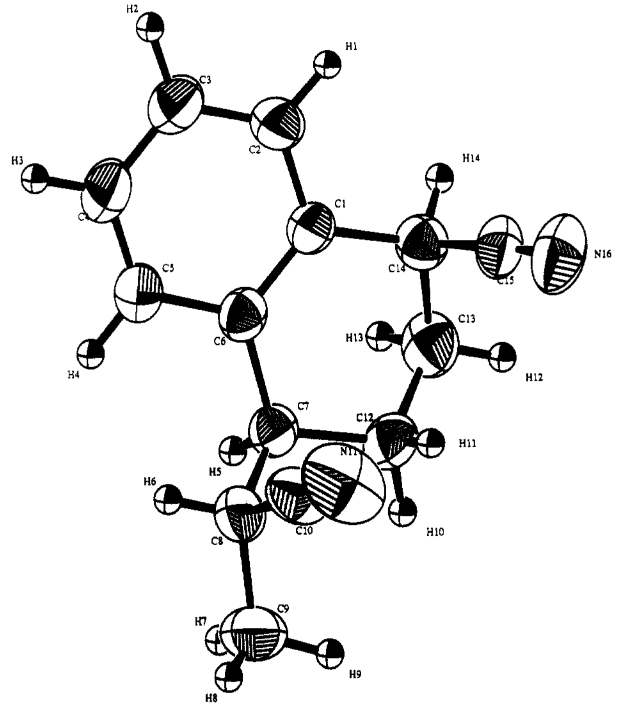


Figure 2. Molecular plot showing the atom labeling scheme and 50% thermal ellipsoids for *cis*-R-THNA.

Final cell parameters (Table II) corresponded to an orthorhombic unit cell. Intensity distribution statistics indicated that the space group was acentric. Systematic absences determined the space group as $Pna2_1$. On the basis of the formula weight and cell volume, there are four molecules per unit cell. From this arrangement, the calculated density is 1.180 g/cm^3. A total of 1246 unique reflections were measured. Of these, 792 (64%) were considered observed with $I > 3\sigma(I)$. These reflections were used for the structure solution and refinement. The structure was solved and refined to $R = 0.034$.[18] The preferred structural solution is *cis*-4-cyano-1,2,3,4-tetrahydro-α(R)-methyl-1-naphthaleneacetonitrile (*cis*-R-THNA) (Table II). A molecular plot showing the atom labeling scheme and 50% thermal ellipsoids for *cis*-R-THNA is shown in Figure 2.

Results and Discussion

The SAn oligomers were vaporized from SAn polymer in vacuo at 240 °C and condensed. Capillary gas chromatographic (GC) analyses of the trimer mixture were unsuccessful in giving complete resolution of all of the components in the mixture (Figure 3). However, the oligomers were separated into groups consisting of the two different types (i.e., An_2S and AnS_2) as indicated by GC–mass spectroscopy. Thus, we turned to high-pressure liquid chromatography (HPLC).

Reversed phase HPLC conditions also gave poor resolution of the oligomers. However, normal-phase HPLC using a cyanopropyl (CN) column gave excellent results. The normal-phase HPLC chromatogram of the oligomers using an IO/THF gradient is shown in Figure 4.

The SAn trimers consisted of mainly the An_2S which elute by HPLC as a cluster of peaks between 12 and 15 min of retention time. The earlier eluting small cluster (6–8-min retention time) is the AnS_2 trimers. The S_3 trimers eluted very early (2–4-min retention time) and were barely detectable. The large difference in polarity between the AnS_2 and the An_2S trimers caused us to attempt solvent

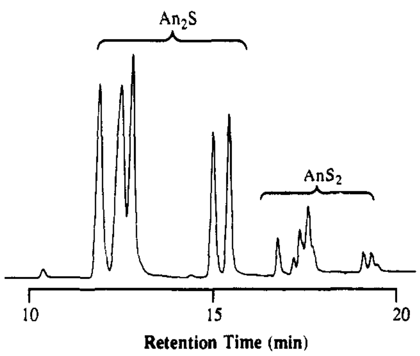


Figure 3. Capillary GC of oligomers vaporized and condensed from SAn.

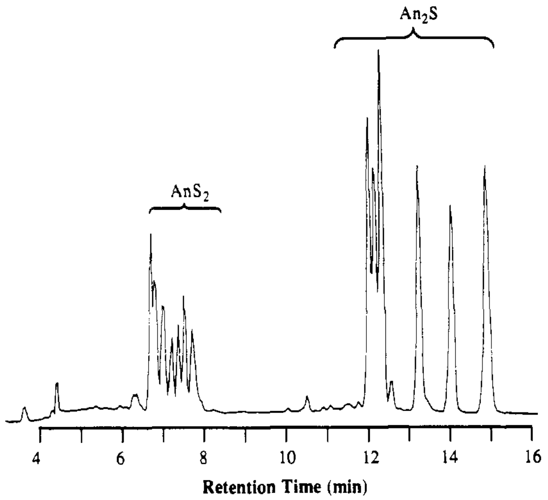


Figure 4. HPLC chromatogram of SAn oligomers.

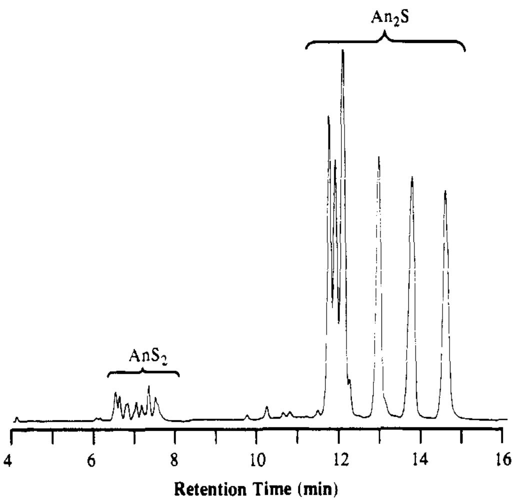


Figure 5. HPLC chromatogram of solvent-fractionated SAn trimers.

extraction of the trimer mixture to remove the AnS$_2$ fraction. Indeed, continuous extraction of the mixture with isooctane allowed the isolation of a >95% pure mixture of An$_2$S trimers. The HPLC chromatogram after solvent extraction is shown in Figure 5.

Upon standing, white crystals began forming in the purified An$_2$S mixture. The crystals were removed by filtration and were found to be the last eluting (i.e., most polar) of the An$_2$S trimers. X-ray crystallography studies showed that the compound was *cis*-4-cyano-1,2,3,4-tetrahydro-α(*R*)-methyl-1-naphthaleneacetonitrile (*cis*-R-THNA). Preparative HPLC was used to further separate the An$_2$S isomers.

The crystals and the An$_2$S preparative LC cuts were analyzed using ^{1}H NMR and ^{13}C NMR. One of the preparative HPLC cuts provided a pure compound, but the rest were mixtures. By comparison of the NMR spectra of the pure materials and the spectra of the mixtures, the structures for all six An$_2$S peaks in the HPLC (Figure 5) were tentatively assigned as shown in Figure 6. The results indicate both diastereomers (cis and trans) of THNP and both cis–trans diastereomer pairs of THNA (*R* and *S*) are formed. The ratio of the three cis–trans diastereomer pairs of isomers THNP/R-THNA/S-THNA is approximately 2:3:2, respectively. Approximately equal amounts of cis and trans isomers are formed within each diastereomer pair.

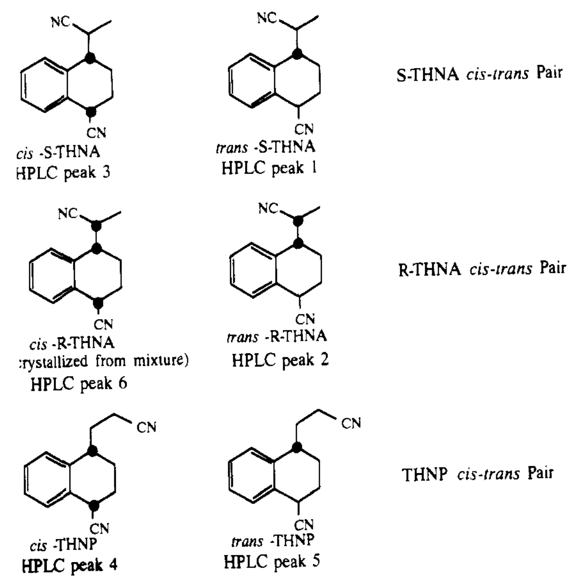


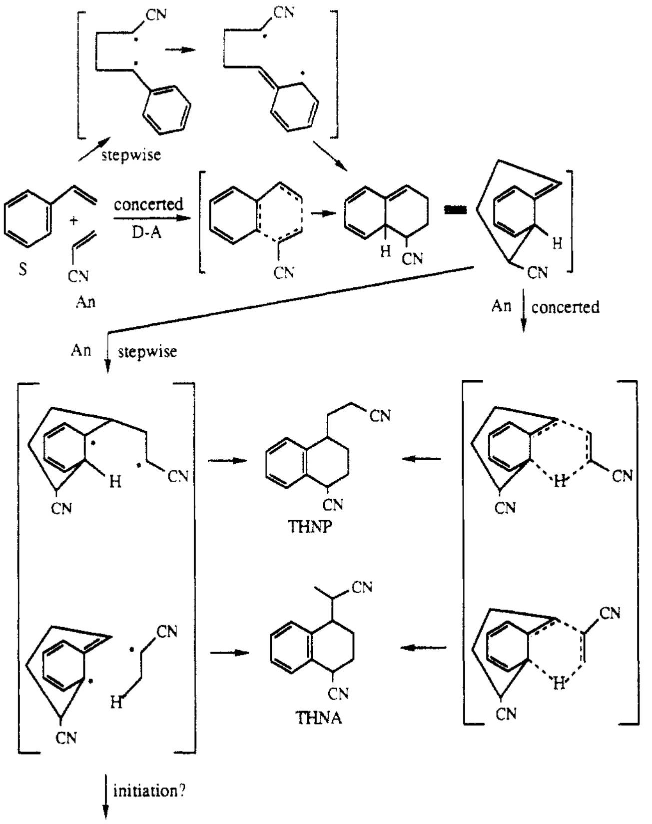
Figure 6. Stereochemistry of the six AN$_2$S trimers from NMR and X-ray crystallography.

These trimer structures arise first from the α regioselective Diels–Alder dimerization of S and An. The dimerization could take place in a concerted or a stepwise manner. The regioselectivity is in agreement with FMO calculations for the concerted process.[19] The addition of another An to form the An$_2$S trimers could occur via concerted or stepwise Alder-ene mechanisms. These processes are summarized in Scheme IV.

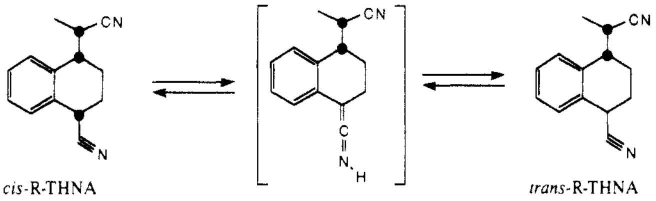
Kirchner and Schlapkohl[15] found about 15% by wt THNP in the An$_2$S trimer mixture, while we found twice that amount. Even though Kirchner and Schlapkohl discuss the formation of THNP in terms of a concerted process, we believe that it could rise via a stepwise process. Hoffmann[16] stresses that the Alder-ene reaction need not necessarily proceed in a concerted fashion if the ene component is geometrically configured such that simultaneous bond-making at its carbon and hydrogen termini is unfavorable, which is likely the case for the styrene–acrylonitrile dimer.

A stepwise Alder-ene process is also likely operative for the formation of the THNA isomers due to the lack of significant stereoselectivity. However, there is the possibility that the An$_2$S trimer ratio is the result of thermal epimerization and thus may not reflect their kinetics of formation but rather the thermodynamics of the structures. To determine if this is likely, we chose to study the rate of thermal epimerization of *cis*-R-THNA in the temperature range of its isolation. This study was accompanied by heating pure crystalline *cis*-R-THNA in a sealed tube (in vacuo) at 230–280 °C and monitoring the rate of stereochemical scrambling at the three stereogenic centers. The results indicate that epimerization at carbon 4 occurs quite rapidly while scrambling at the 1 and α carbons takes place relatively slowly. The rate difference is likely

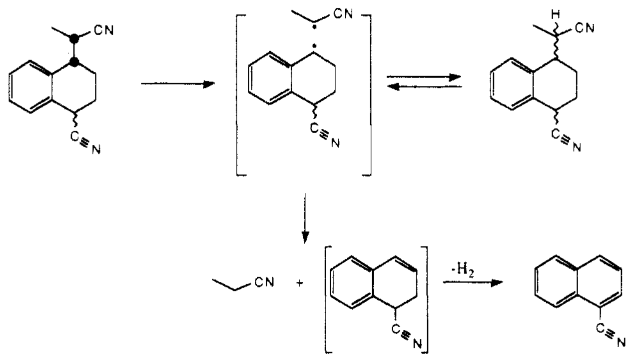
Scheme IV
Possible Mechanisms of Formation of An_2S Trimers



Scheme V
Mechanism of Epimerization of *cis*-R-THNA to *trans*-R-THNA



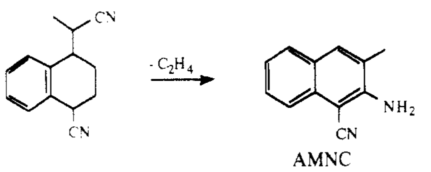
Scheme VI
Homolysis/Radical Recombination Mechanism for Epimerization at the 1 and α Carbons



due to tautomerization of the 4-cyano group to produce a ketenimine conjugated with the phenyl ring (Scheme V), whereas tautomerization of the α-cyano group does not have a conjugative driving force.

Epimerization at the other stereogenic centers may involve a bond homolysis/radical recombination mechanism (Scheme VI), since the formation of propionitrile and α-cyanonaphthalene was detected by GC-MS, ^1H, and ^{13}C NMR analyses.

Scheme VII
Rearrangement of *cis*-R-THNA upon Heating



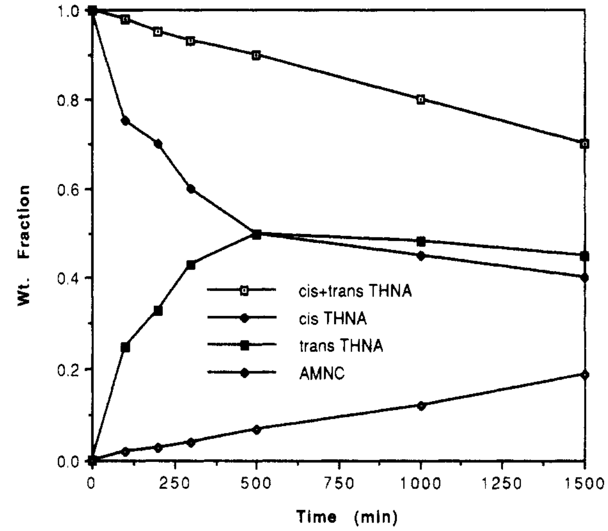


Figure 7. Epimerization and rearrangement kinetics of *cis*-R-THNA at 265 °C.

The actual rate data for epimerization of *cis*-R-THNA are complicated by a simultaneous facile rearrangement (Scheme VII) to form 2-amino-3-methyl-1-naphthalenecarbonitrile (AMNC). The mechanism and kinetics of this novel rearrangement will be the subject of a separate paper.

Figure 7 shows that the rate of epimerization at carbon 4 at 265 °C was faster than the simultaneous rearrangement (i.e., by the time the epimerization had reached equilibrium, ~10% w/w had rearranged to AMNC) but epimerization kinetics at the 1 and α carbons is much slower.

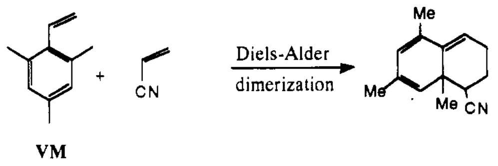
Since the An_2S trimer syrup was collected in a continuous process having an average residence time of only a few minutes at 240 °C, it is unlikely that significant thermal epimerization occurred.

The question still remains whether the radical intermediates during the proposed stepwise formation of the An_2S trimers are responsible for initiating SAn copolymerization. If they are the main source of initiating radicals, the addition of reagents that catalyze aromatization of the Mayo triene dimer (radical precursor) should slow the polymer initiation rate. As mentioned earlier, in spontaneous styrene homopolymerization in the presence of camphorsulfonic acid (CSA), and "Mayo styrene dimer" responsible for radical generation is mostly aromatized without the formation of radicals, thus resulting in significant polymerization rate retardation.[11,12] However, addition of CSA to SAn copolymerization had no effect on the polymerization rate.

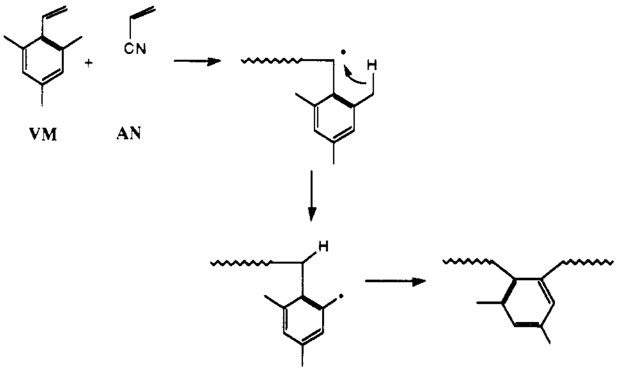
Furthermore, we discovered that a mixture of 80/20 w/w 2-vinylmesitylene/An (VMAn) spontaneously copolymerizes when heated at 150 °C for 22 h (total monomer conversion was 16%). The Diels–Alder dimer between VM and An cannot initiate polymerization by the Mayo mechanism due to the lack of the annular hydrogen atom (Scheme VIII). Since VM and An cannot spontaneously copolymerize by the Mayo mechanism, any formation of polymer must be by another mechanism.

Characterization of the VMAn copolymer by DSC, GPC, and ^{13}C NMR showed that it had a glass transition tem-

Scheme VIII
Diels–Alder Dimer between VM and An



Scheme IX
Potential IMCT Mechanism for VMAn Formation



perature of 135 °C and a MW of 100 000 and contained 33% w/w AN.

Polymer formation from VM by a free radical mechanism is surprising since the vinyl group is extremely hindered by the ortho methyl groups and should be forced out of the plane of the ring. This would lead to less orbital overlap with the phenyl ring, destabilizing the radical transition state. One possibility is that the VMAn copolymer was produced via an intramolecular chain transfer (IMCT) mechanism[20] (Scheme IX). However, ^{13}C NMR analysis of the VMAn copolymer showed that the polymer backbone had the expected 1,2-vinyl structure rather than an *o*-phenylene structure which would result if IMCT had taken place.

Conclusions

Six An_2S trimers are formed during the spontaneous copolymerization of S and An. They are the four THNA and the two THNP diastereomers. These trimers are likely formed via stepwise Alder-ene reactions due to the geometry of the styrene–acrylonitrile Diels–Alder dimer. Furthermore, the Alder-ene reactions proceed without significant stereoselectivity, again suggesting stepwise processes.

It is unlikely that radical intermediates, formed during the stepwise Alder-ene reactions of the styrene–acrylonitrile Diels–Alder dimer, are responsible for initiation of SAn copolymerization. This conclusion is reached because the addition of an acid catalyst known to deactivate the Mayo styrene dimer, responsible for initiating radical formation is S homopolymerization, had no effect on the rate of SAn copolymerization. Furthermore, a styrenic monomer (VM) incapable of polymerizing by the Mayo mechanism was found to spontaneously copolymerize with acrylonitrile. Together, these findings lead us to conclude that the Mayo mechanism is not the main mechanism for generating radicals responsible for initiation of SAn polymerization. A major problem, however, with the Flory alternative mechanism for SAn initiation is that 1-phenyl-2-cyanocyclobutane (a byproduct of the Flory tetramethylene diradical mechanism) is yet to be found in SAn. It is possible that 1-phenyl-2-cyanocyclobutane forms but does not survive under the polymerization conditions.

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