dimerized anthracene groups upon exposure to air and laboratory lighting. Further, it was shown that treatment of these polymers with CF_3COOH in $CHCl_2$ can lead to an increase in the anthracene content of the insoluble products.

Of the three vinylanthracene monomers, the 2-vinyl isomers have the greatest tendency to polymerize by all three mechanisms of initiation. The major obstacle to achieving high molecular weight products in the free radical and cationic polymerization is the extremely low solubility of the monomers in suitable solvent systems. The carbanions from 2VA and 2P2A are relatively stable at low temperatures and anionic polymerization gives high yields of high molecular weight polymers.

High molecular weight polymers of 1-vinylanthracene can be achieved by anionic polymerization. The carbanion is much less stable than that from 2VA, but the higher solubility of the monomer results in higher reaction rates at low temperatures. 2-Propenyl-1-anthracene could not be polymerized by ionic methods.

In spite of rigorous purification, 9-vinyl- and 9-vinyl-10-methylanthracene did not yield high molecular weight polymer by radical or ionic polymerization. The carbanions formed even at low temperatures, < -60 °C, appear to be highly unstable and undergo some transformation to a less active species. Cationic polymerization gave the highest molecular weights, $\overline{M}_w \approx 20\,000$, $\overline{DP} \approx 100$.

Spectroscopic characterization of the 1- and 2-vinylanthracene polymers was fully consistent with a conventional 1,2-vinyl structure. The incorporation of anthracene rings into the polymer chains through spurious addition/transfer reactions cannot be totally ruled out but these are not significant contributions to the polymerization reaction. Similarly, poly(9-vinyl-10-methylanthracene) appears to have a conventional structure. The 9-vinylanthracene polymers synthesized in this work also possess predominantly 1,2-vinyl structures, provided polymerization and characterization precautions have been followed. In our opinion, there is no need to invoke the anomalous 1,6 polymerization mechanism proposed by other workers. It is clear, however, that the free radical and ionic polymerization of the 9-vinylanthracene monomers is considerably more complex than the corresponding 1- and 2-vinyl series. This arises most probably from the extremely low solubility of the monomer and the extreme instability of the propagating species. The mechanistic issues will be covered in the following paper.[14]

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Polymerization of Vinylanthracene Monomers. 4. A Spectroscopic Study of the Anionic Polymerization of 1-, 2-, and 9-Vinylanthracenes

J. F. Yanus, M. Stolka, and J. M. Pearson*

Xerox Corporation, Research Laboratories, Webster, New York 14580.

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ABSTRACT: A spectroscopic investigation of the anionic polymerization of a series of 1-, 2-, and 9-vinylanthracene monomers has been carried out. The spectra of the corresponding polymeric carbanions are reported and substantiated where possible using nonpolymerizable model compounds. It was established that the carbanions produced from the 2-vinylanthracenes are more stable than those from the 1- and 9-vinyl monomers. This can be rationalized in terms of steric factors within the molecules which permits greater degrees of resonance stablization in carbanions from the 2-substituted series. The polymerization characteristics of the monomers are consistent with the spectroscopic/stability observations.

The free radical and ionic polymerization reactions of 9-vinylanthracene were studied by Rembaum,[1] Michel,[2] Bergmann,[3] and Katz[4] and more recently by Shelekhov[5] and Marechal.[6] The polymerization characteristics of the corresponding 1- and 2-vinylanthracene monomers have also been reported.[3,4a,6] In all instances the investigators reported the difficulties associated with achieving high molecular weight products and these polymerization systems have remained a paradox.

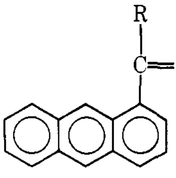
The anionic polymerization of 9-vinylanthracene was studied by Rembaum[1b,c] and Michel.[2b] Both authors concluded that the polymerization is dominated by transfer reactions involving the anthracene ring leading to oligomeric products with unusual structures. The structure of the propagating carbanion species was not established although reference was made to a green color persisting throughout the reaction. Szwarc[7] has summarized the findings and in addition to electron transfer complications has proposed a "wrong" monomer addition to account for the experimental results. Most of the evidence for the currently accepted polymerization mechanism comes from the analysis of the product polymers and it is clear that a more direct investigation is essential.

In several recent publications[8–10] we reported the successful ionic polymerization of a number of 1-vinyl- and 2-vinylanthracene monomers into high molecular weight polymers with conventional structures. The details of the monomer synthesis and purification and of the ionic polymerization techniques have also been presented in these publications. In this paper we present the spectroscopic analysis of the reactions and discuss the mechanistic issues along with some parallel studies of the related 9-vinylanthracene monomer systems.

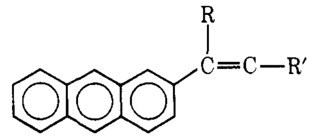
Experimental Section

The monomer synthesis, purification, and handling were the most critical aspects of this work. The synthetic and polymerization procedures are covered in detail in parts 2[9] and 3[10] of this series.

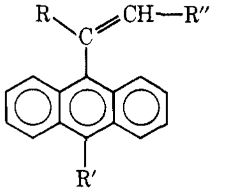
Monomer Synthesis. The syntheses of the 1-vinylanthracene monomers, 1 and **1a**, the 2-vinylanthracene monomers, **2** and **2a**, and the 9-vinylanthracene monomers, **4** and **5**, were described previously.[9,10] In an effort to elucidate the nature of the carbanions produced in the polymerization, a number of model compounds were synthesized.



1, R = H
1a, R = CH_3

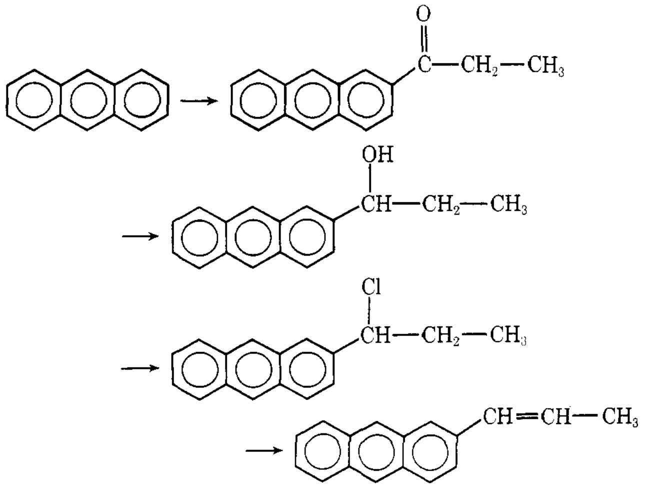


2, R, R′ = H
2a, R = CH_3; R′ = H
3, R = H; R′ = CH_3



4, R, R′, R″ = H
4a, R = CH_3; R′, R″ = H
5, R, R″ = H; R′ = CH_3
6, R, R′ = H; R″ = CH_3

1-Propenyl-2-anthracene (**3**) was prepared from 2-anthryl ethyl ketone by the following reaction sequence,



2-Anthrylethylketone. Anthracene (150 g) was dispersed into 150 ml of nitrobenzene and the solution was purged with nitrogen. In a separate vessel 255 g of $AlCl_3$ was dissolved in 150 ml of nitrobenzene and 150 ml of propionic anhydride was added slowly. The $AlCl_3$/propionic anhydride complex was added slowly to the anthracene dispersion at a temperature of 15 °C. The mixture was agitated for 15 h and the slurry was subsequently treated with 1 l. of cold benzene (dried over $MgSO_4$) and allowed to stand for 5 h. The red complex was filtered and washed with benzene and hexane. After hydrolysis of the complex with ice/HCl the product was filtered and recrystallized from benzene to yield 30 g (15%) of pale yellow crystals, mp 155 °C.

1-Propanol-2-anthracene. 2-Anthryl ethyl ketone (25.5 g) was dispersed in 1.5 l. of ethanol and refluxed under nitrogen. Addition of 25 g of $NaBH_4$ in 280 ml of water was followed by reflux of the mixture for 2 h. Approximately ⅔ of the ethanol was removed by distillation and the product was precipitated by treatment with ice/HCl. Recrystallization from benzene/methanol (1:1) gave 10 g (40%) of a white crystalline material, mp 135 °C.

1-Propenyl-2-anthracene. Propanol (9 g) was converted to the corresponding chloride by treatment in refluxing benzene (100 ml) with thionyl chloride (20 ml). Following precipitation with petroleum ether the product was crystallized from hexane/benzene (1:1) to give 4.5 g (46%) of chloride, mp 155–156 °C. Chloride (3.9 g) was dissolved in DMF containing 4 g of finely dispersed Li_2CO_3 and heated to 130 °C under nitrogen for 5 h. The product was isolated by precipitation into water, washed with dilute HCl and water, and dried. Recrystallization from ethanol/benzene (5:1) followed by chromatographic purification (Woehlm neutral alumina) gave a white crystalline material, mp 191.5 °C. Insolubility problems precluded an NMR analysis of this compound.

2-Propenyl-9-anthracene (4a). All attempts to prepare this monomer from 9-acetylanthracene or 9-anthracenecarboxaldehyde were unsuccessful.

1-Propenyl-9-anthracene (6) was prepared from 9-anthracenecarboxaldehyde via the Wittig procedure. A solution of 18.6 g (0.05 mol) of triphenylmethylphosphonium bromide was treated with butyllithium as described earlier.[9,10] Addition of a THF solution of aldehyde (10.3 g in 50 ml), followed by reflux and hexane treatment, gave the product. Chromatographic purification and recrystallization from hexane/benzene (9:1) gave pale yellow needle shaped crystals: mp 79–80 °C; NMR ($CDCl_3$) δ 1.8–2.1 (m, 3, CH_3), 5.4–6.1 (m, 1, —CH=), and 6.7–8.2 ppm (m, 10, aromatic + —CH=).

Monomer Purification. Prior to anionic polymerization, the monomer was recrystallized from carefully deoxygenated solvents under an inert atmosphere in subdued light. The material was then column chromatographed under an inert atmosphere in the dark using Woehlm neutral alumina conditioned and eluted with deoxygenated solvents (hexane). Recovered monomer (vacuum evaporation of solvent) and monomer solutions were subsequently handled in darkened vacuum ampules or stored under vacuum in a refrigerator.

Anionic Polymerizations. Polymerization reactions were carried out using standard vacuum manipulative techniques. As far as possible, the prepolymerization functions were carried out in subdued lighting. Reactions were run in sealed ampules in appropriate temperature controlled baths and spectroscopic analyses were performed using a CARY 14 spectrophotometer fitted with a low temperature optical Dewar. The vinylanthracene carbanions were monitored following addition of a slight excess of monomer to the initiator solutions or during an actual polymerization run.

Results

Attempts to polymerize the 1-, 2-, and 9-vinylanthracene monomers with typical electron transfer type initiators, e.g., sodium biphenyl and sodium naphthalene, in the temperature range −80 to +25 °C were completely unsuccessful. On the other hand, addition type initiators, e.g., living polystyrene ($\sim\!S^-$) and the α-methylstyrene tetramer dianion $(\alpha MeS_4)^{2-}$, gave reproducible polymerization reactions and products with 1- and 2-vinylanthracenes.

2-Vinylanthracenes. Addition of both 2-vinylanthracene (**2**) and 2-propenyl-2-anthracene (**2a**) to a THF solution of the initiator at −78 °C results in immediate formation of a bright purple color. The spectrum of the living carbanion of (**2**) ($\sim\!2VA^-$, Na^+) is shown in Figure 1. Absorption maxima around 550 nm ($\epsilon = 1.9 \times 10^4$), 500 nm ($\epsilon = 1.7 \times 10^4$), and 460 nm ($\epsilon = 9 \times 10^3$) with a long wavelength shoulder at 580 nm characterize this polymeric carbanion. The spectrum of the

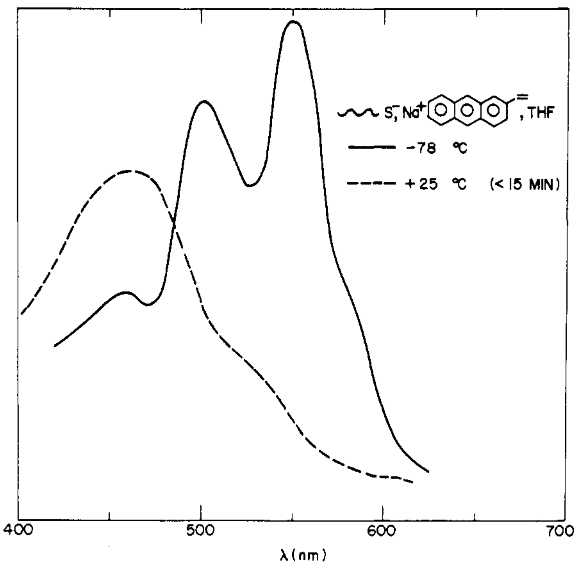
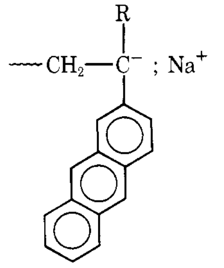


Figure 1. Optical spectrum of the carbanion formed from 2-vinylanthracene.

polymeric anion of **2a** is very similar to that from **2** with an absorption maximum at 520 nm ($\epsilon = 2.0 \times 10^4$) with shoulders around 560 and 480 nm.

The low temperature spectra have been assigned to the conventional vinyl monomer carbanions,



This assignment is substantiated by analysis of the spectrum of the carbanion formed from the nonpolymerizable model compound, 1-propenyl-2-anthracene (**3**). The spectrum of the product resulting from addition of **3** to ~~~S⁻ is presented in Figure 2. At −78 °C the absorption bands are present at 550 nm ($\epsilon = 6 \times 10^3$), 500 nm ($\epsilon = 1.6 \times 10^4$), and 470 nm ($\epsilon = 1.1 \times 10^4$).

Increasing the temperature results in a rapid change in the three spectra and development of a brown color at ambient temperature. In all cases warming produces some species with an absorption band around 460 nm, with a molar extinction coefficient estimated at 1.5×10^4, assuming all the living polymer anions convert. The living polymer from **2a** is somewhat more stable than **2.**

The polymeric anions are stable at temperatures below −50 to −60 °C but undergo some decomposition/rearrangement at higher temperatures. Figure 3 shows the effects of warming the anion **2** to −30 °C, holding at this temperature for 15–30 min, and recooling to −78 °C. There is an indication that the transformation is partially reversible. Recooling solutions warmed to −10 to +20 °C does not restore any of the original spectrum. The nature of this final species, λ_{max} ~460 nm, has not been clarified. Reaction of **2** or **2a** directly with the initiator at temperatures above −20 °C results immediately in formation of this species.

At temperatures below −50 °C the anionic polymerization of **2** and **2a** proceeds essentially to completion and high molecular weight products are formed. The reaction times are long because of monomer insolubility, and the molecular weight distributions tend to be higher than those normally encountered in an ideal anionic polymerization system. Distributions $\gtrsim 2$ have been found for $\bar{M}_n > 10^4$–10^6. Within the temperature range −50 to −30 °C, intermediate polymer conversions and much lower molecular weights, $\bar{M}_n < 10^4$, were obtained. At temperatures higher than −30 °C virtually no polymer is formed. It has also been shown that the species absorbing at 460 nm does not effectively initiate the polymerization of **2** or **2a** even at −78 °C.

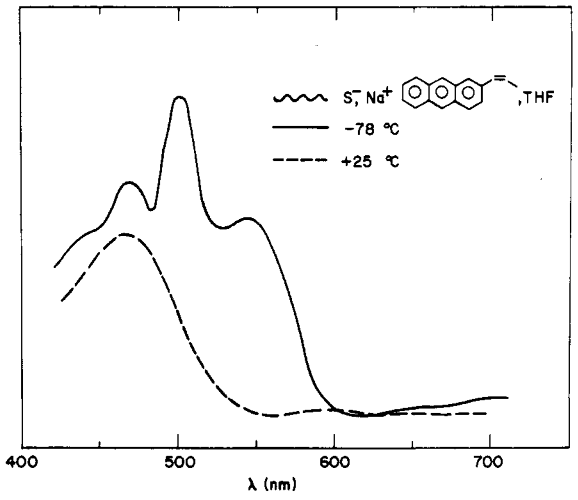


Figure 2. Optical spectrum of the carbanion formed from 1-propenyl-2-anthracene.

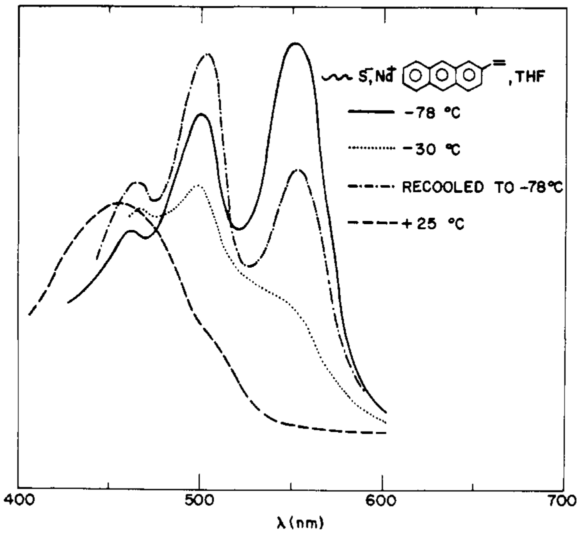


Figure 3. Optical spectrum of the carbanion formed from 2-vinylanthracene; effect of temperature.

The carbanions from **2** and **2a** are stable enough at −78 °C to effect a block copolymer synthesis by sequential monomer addition. This was clearly demonstrated for styrene, but this aspect of the system was not pursued any further.

1-Vinylanthracenes. 1-Vinylanthracene (**1**) reacts with addition type initiators in THF at −78 °C to produce a dark green colored solution with absorption bands around 590 nm ($\epsilon \sim 10^2$) and 460 nm ($\epsilon \sim 2.0 \times 10^4$) (Figure 4). Upon warming the solutions rapidly convert to orange-brown, λ_{max} ~450 nm. Polymerization is effective only at low temperatures and high molecular weights can be attained. Reaction of **1a** with addition type initiators results in the immediate formation of an orange-brown colored solution even at temperatures as low as −80 °C. The absorption maximum occurs at 460 nm ($\epsilon \sim 1.6 \times 10^4$, assuming the initiator is all converted to the ab-

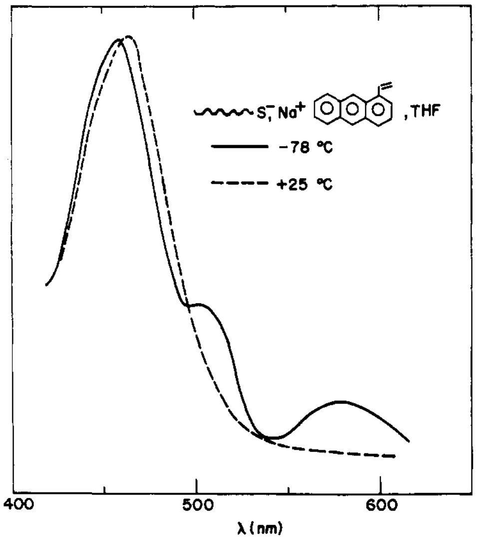


Figure 4. Optical spectrum of the species formed in the reaction of 1-vinylanthracene with "living" polystyrene in THF.

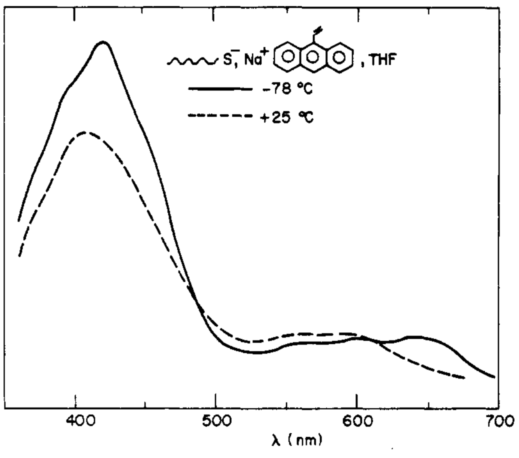


Figure 5. Optical spectrum of the species formed in the reaction of 9-vinylanthracene with "living" polystyrene in THF.

sorbing species). No polymer was obtained from this system.

Assuming that the species with an absorption band at 590 nm is the conventional polymer carbanion ($\sim$1VA$^-$), it is clear that this species is much more unstable than the corresponding anions from **2** and **2a**. Even at low temperature, no absorption maxima beyond 460 nm were observed for **1a**, indicating that the anion from this monomer is highly unstable. Initiation is effective but the anion apparently rearranges/decomposes immediately and no polymerization occurs.

9-Vinylanthracenes. Addition of 9-vinylanthracene (**4**) to a solution of αMeS_4^{2-}, $2Na^+$ in THF at −78 °C resulted in immediate formation of a green color. The spectrum is shown in Figure 5 and exhibits a maxima at 420 nm ($\epsilon = 2.3 \times 10^4$) with a broad band at longer wavelengths ~600 nm ($\epsilon = 2.3 \times 10^3$). The molar extinction coefficients are calculated from the initiator concentration assuming formation of one product species. Upon warming, the anion from **4** undergoes a definite spectral change, with loss of the long wavelength absorption bands, although the solution remains green in color. The 9-vinyl-10-methylanthracene monomer (**5**) system exhibits an identical behavior.

The spectrum of the model 9-anthrylmethide anion has been reported,[11] λ_{max} 715, 675 nm ($\epsilon = 6 \times 10^3$), and 470 nm ($\epsilon = 1.2 \times 10^4$), in THF at 25 °C. The nonpolymerizable model compound (**6**), 1-propenyl-9-anthracene, gives rise to the anion whose spectrum is shown in Figure 6. This spectrum exhibits maxima at 690 nm ($\epsilon = 6 \times 10^2$), 645 nm ($\epsilon = 5 \times 10^2$), and 460 nm ($\epsilon = 4 \times 10^3$) and is surprisingly different from that of the 9-anthrylmethide anion. The anion is unstable at temperatures above −50 °C and the spectrum of the final product is very similar to that produced from **4** and **5**.

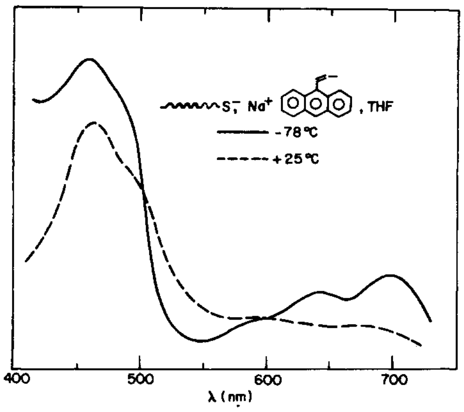


Figure 6. Optical spectrum of the species formed in the reaction of 1-propenyl-9-anthracene with "living" polystyrene in THF.

All attempts to polymerize **4** and **5** to high molecular weight were unsuccessful. Conversions varied and the maximum values of $\overline{M}_n$ achieved were in the range 10^3.

Discussion

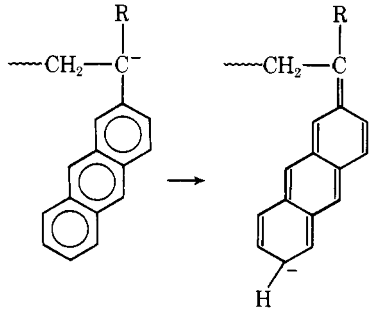
Of the three vinylanthracene monomers, only the 1- and 2-vinylanthracenes can be polymerized by anionic addition type initiators to high molecular weight polymers. The polymeric carbanions are stable only at low temperatures, <−50 °C, and reactions conducted above this temperature become complex with yields and molecular weights decreasing rapidly. In the case of the 9-vinylanthracenes it was not possible to attain molecular weights ($\overline{M}_n$) greater than 10^3–10^4.

The need to carry out the polymerization reactions at low temperature, plus the extremely low solubility of the vinylanthracene monomers, makes these very unusual anionic polymerizations. The concentration of monomer in solution is low (estimated at <0.05 wt % for **2** in THF at −78 °C) and is replenished from the insoluble monomer particles present. It appeared from visual observations that the polymerization process occurred in solution rather than on the solid monomer particles which remained white throughout the polymerization. Certainly at the completion of the reaction the system was completely homogeneous and, in fact, the disappearance of the solid monomer provides some crude measure of the conversion. In our judgement, therefore, although the reacting system is heterogeneous, the polymerization is a homogeneous one.

In view of the unusual nature of these polymerizations, it was impossible to obtain any meaningful kinetic data. The reaction appears to be governed by the concentration of monomer in solution, and this will be controlled by the particle size of the insoluble monomer, stirring rate, etc. Within the initiator concentration range investigated (10^{-3} to 10^{-5} mol/l.) the initiation reaction appears to be rapid. In the experimental unit employed, the spectrum can be recorded 5–15 s after mixing the reagents. Initiation, as measured by the transformation of the αMeS_4^{2-} spectrum into that of the polymer anion, is complete within this time period.

The achievement of high molecular weight polymers ($\overline{M}_n > 10^5$) tends to support the argument that the propagation reaction occurs in a homogeneous medium. The alternative proposition that chain growth on the solid monomer phase is followed by dissolution of the living polymer anions is not supported by the spectroscopic data which show that the spectrum remains essentially constant during the polymerization. The broad molecular weight distributions, $\overline{M}_w/\overline{M}_n \gtrsim 2$, are not typical of an ideal anionic polymerization. However, the long reaction times (days) and the intrinsic instability of the propagating carbanions would tend to increase the probability of spurious termination/transfer processes which would broaden the distribution. The participation of chain/electron transfer reactions or inverse monomer addition cannot be completely ruled out and in fact these complications may become important at elevated temperatures.

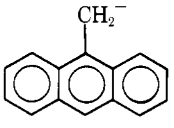
The carbanions produced from the 2-vinylanthracenes were more stable than those from the 1- and 9-vinyl series. The spectral assignment of the living polymer anions from **2** and **2a** was substantiated by the model compound **3**. All these carbanion species are unstable at temperatures above −50 to −60 °C, transforming into some species which is a very ineffective initiator for the polymerization of the monomer. Figure 3 shows the effect of warming a solution of the anion from **2** and subsequently recooling to −78 °C. Warming from −78 to −30 °C and maintaining the solution at this temperature for 15–30 min produces a significant decrease of absorption of the original spectrum. Recooling to −78 °C partially restores the original spectrum. Solutions brought to temperatures higher than −30 °C show very little recovery. The anion from **2a** is more stable than that from **2** and longer exposure to elevated temperatures is required to irreversibly destroy the active species. These spectral changes on warming the solutions have not been elucidated. The ultimate product is a colored species with a strong absorption at 460 nm, $\epsilon \sim 1$ to 2×10^4, and it is tempting to attribute this to some ring type carbanion, e.g.,



The absorption spectra of the 9,10-dihydroanthracene and 9-alkyl-9,10-dihydroanthracene anions have been reported previously,[12] λ_{max} 425–455 nm ($\epsilon = 1.8 \times 10^4$, THF, Na^+). Also, the adducts formed between, for example, the anion of styrene and α-methylstyrene and anthracene absorb at 440 nm ($\epsilon = 2.7 \times 10^4$) and 450 nm ($\epsilon = 2.5 \times 10^4$), respectively.

The 1- and 9-vinylanthracene systems exhibit a very different behavior from the 2-vinylanthracenes. In the case of the 1-vinyl monomers, the spectroscopic results indicate formation of some species with a strong absorption at 460 nm and much weaker absorption bands in the 500–600 nm region. At elevated temperatures only the 460 nm peak is present. Polymerization occurs only at low temperatures and high molecular weights are produced. No polymer is formed at elevated temperatures. A very similar series of spectra were recorded for the 9-vinylanthracene anions. However, even at low temperatures only low molecular weight polymers could be isolated. For both monomer systems, the species responsible for the long wavelength bands is very unstable and the reversibility phenomenon encountered in the 2-vinylanthracenes is not observed.

One of the puzzling features uncovered in this study is the different spectral and stability characteristics of the model anions of the 9-vinylanthracene system (Figure 6 and ref 11).



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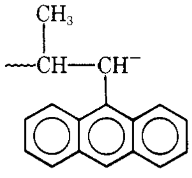

8

The simple arylmethide anion (**7**) is stable at room temperature, where **8** decomposes rapidly at temperatures above −50 °C. This observation can be rationalized from a consideration of steric factors in the molecules. Steric hindrance from hydrogen atoms in the 1 and 8 positions prohibits coplanarity of the olefin group in **6** with the anthracene ring. The carbanion **8**, therefore, is not stabilized by resonance with the anthracene group, whereas this stabilization can readily occur in the unhindered anion **7**. The effect can be clearly demonstrated with space filling models.

This argument can be extended to the carbanions formed from both the 1- and the 2-vinylanthracenes. In the 1-substituted systems the steric constraints from the 9-H are also severe. However, with the 2-substituted derivatives, steric factors are greatly reduced and much higher degrees of resonance stabilization with the anthracene ring can be achieved. This explains the trends observed in the anionic polymerizability of the three monomers; 2-vinylanthracenes can be polymerized more readily and cleanly than the 1-vinylanthracences, while the 9-vinylanthracenes do not give polymers of any reasonable molecular weight. In the 9-vinylanthracene system the propagating carbanions are too unstable, even at low temperature, and complex polymerizations and products result. The 1-vinylanthracene case is intermediate between the 2- and the 9-substituted monomers.

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