Polymerization of Vinylanthracene Monomers.
3. 1- and 9-Vinylanthracenes

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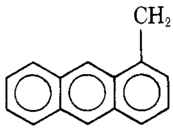
ABSTRACT: The synthesis and the free radical, anionic, and cationic polymerizations of a series of 1- and 9-vinylanthracene monomers have been investigated. High purity 1-vinylanthracene can be polymerized to a high molecular weight linear polymer ($\overline{M}_n \approx 8 \times 10^4$) by anionic addition-type initiation at low temperatures. Since the monomer purity is extremely important in attaining high molecular weight, the polymerization of 9-vinylanthracene and its 10-methyl derivative has been examined using rigorously purified monomers. In spite of rigorous purification, neither monomer yields high molecular weight polymer by radical or anionic polymerization. The cationic polymerization gave the highest molecular weight, $\overline{M}_w \approx 2 \times 10^4$.

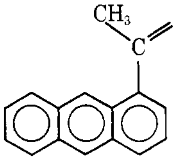
In part 1 of this series[1] we reported the synthesis of high molecular weight polymers of some anthracene containing monomers and in part 2[2] we described in detail the synthesis and polymerization of 2-vinyl- and 2-propenyl-2-anthracene. It was demonstrated that successful polymerization requires monomer of very high purity. These monomers behave as conventional vinyl monomers producing linear soluble polymers with no evidence for across-the-ring propagation observed with 9-vinylanthracene.[4] Synthesis of soluble polymers with molecular weights up to 10^5–10^6 was possible in spite of very low solubility of both 2-vinylanthracene and 2-propenyl-2-anthracene under the conditions of the polymerization.

In this paper we discuss in detail the synthesis and polymerization of 1-vinylanthracene (**1**) and its α-methyl analogue (**2**). As was reported previously,[1] 1-vinylanthracene could also be polymerized to a high molecular weight soluble polymer. Considering the success in polymerizing 1-vinyl- and 2-vinylanthracene monomers we decided to reinvestigate the polymerization of 9-vinylanthracene (**3**) and its 10-methyl derivative (**4**) with particular emphasis on monomer purity and polymerization conditions. These monomers are known.



1

1-vinylanthracene (1-VA)



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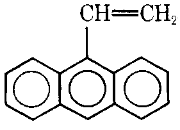
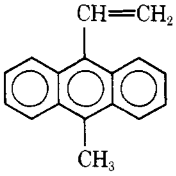
2-propenyl-1-anthracene (2P1A)



3

9-vinylanthracene (9-VA)



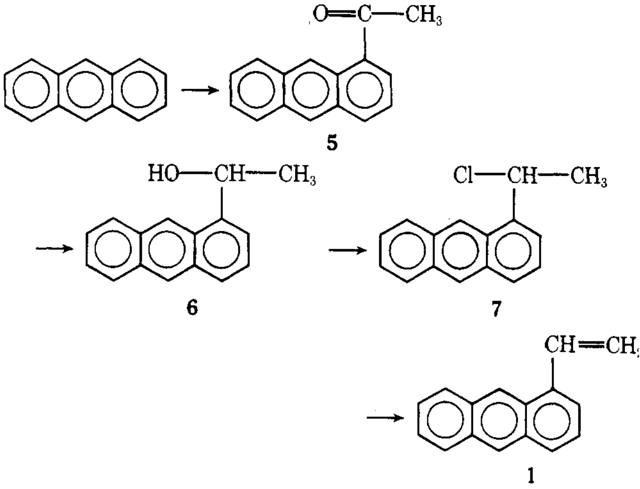
4

9-vinyl 10-methylanthracene (9-V10MeA)

The polymerization of **3** has been studied extensively[5-7] but only some conversion datum is available on the radical polymerization of **1**.[8] The polymerization of **4** was reported previously by us[3] and two recent publications have emerged.[7,9] It can be concluded from these investigations that only very low molecular weight polymer products were achieved with no information on mechanistic issues.

Experimental Section

Synthesis of 1-Vinylanthracene (1). 1 was synthesized by acetylation of anthracene in the 1 position followed by reduction of the ketone to alcohol, conversion to the corresponding chloride, and dehydrochlorination in a basic medium:



1-Acetylanthracene (5). Anthracene, (18 g; 0.10 mol) is stirred in 300 ml of methylene chloride in an ice bath under a blanket of argon. In a separate flask, 8.6 ml (0.12 mol) of acetyl chloride is slowly added to 26 g (0.2 mol) of aluminum chloride in 180 ml of methylene chloride. The pale greenish mixture of the $AlCl_3/CH_3COCl$ complex with uncomplexed $AlCl_3$ is slowly added to the anthracene dispersion over a period of 30 min. After 2 h at 0 °C the red solid complex is filtered out, washed with methylene chloride and hexane, and hydrolyzed in ice/HCl. The product was recrystallized from ethanol to yield 12.0 g (55%) of yellow crystalline **5**, mp 106–107 °C (lit. 107.5–109 °C;[10] 110.5–111 °C[11]).

1-(1-Anthryl)ethanol (6) was synthesized by reduction of 10 g of **5** with sodium borohydride using the procedure described in part 2[2] for 1-(2-anthryl)ethanol. Yield 7.0 g (69%); mp 106–107 °C (lit. 114–115 °C;[12] 116–118 °C[10]).

1-(1-Anthryl)-1-chloroethane (7) was synthesized from 6.5 g of **6** by reaction with thionyl chloride according to the procedure described in part 2[2] for the synthesis of 1-(2-anthryl)-1-chloroethane. Yield 6.0 g (85%); mp 59–60 °C.

1-Vinylanthracene (1) was synthesized by dehydrochlorination of 5.5 g of **7** in Li_2CO_3/DMF using the procedure described in part 2[2] for the synthesis of 2-vinylanthracene. Yield 4.0 g (86%); mp 61 °C (lit. 58–61 °C[9]); NMR ($CDCl_3$) δ 5.32–5.36, 5.50–5.53, 5.58–5.61, 5.86–5.90 (q, 2, =CH_2), 7.14–7.36 (q, 1, —CH=), and 7.74–8.60 ppm (m, 9, aromatic).

Synthesis of 2-Propenyl-1-anthracene (2). The monomer was synthesized from 1-acetylanthracene (**5**) by the Wittig procedure. To a solution of 64 g of triphenylmethylphosphonium bromide (0.18 mol) in 300 ml of THF (N_2 blanked) is slowly added 85 ml of *n*-butyllithium in hexane (~0.2 mol). The orange-red solution is stirred for 1 h and then 33 g (0.15 mol) of **5** in 150 ml of THF is added in small portions. After addition is complete, the reaction mixture is brown/yellow and heterogeneous. The mixture is refluxed for ~18 h. After cooling, 0.5 l. of hexane is added, the precipitate is filtered, and the liquid portion is evaporated and chromatographed on basic alumina (Woelm). Hexane and hexane–benzene 4:1 were used as eluents. After evaporation of the eluent, the colorless oil slowly crystallized at −30 °C to

Table I
Acetylation of Anthracene in the Presence of $AlCl_3$[b]

Main product	Solvent	Acetylating agent	Preferred temp, °C	Anthracene	Acetylating agent	$AlCl_3$	Approx yield of purified product, %
1-Acetylanthracene	CH_2Cl_2	CH_3COCl	0	1	1	2	60
9-Acetylanthracene	CH_2Cl_2[a]	CH_3COCl	<0	1	1	1	60
2-Acetylanthracene	Nitrobenzene	$(CH_3CO)_2O$	15	1	0.75[a]	2.2	60
1,5-Diacetylanthracene	CH_2Cl_2	CH_3COCl	0	1	2	4	50

[a] Effectively, 1.5 mol of acetyl groups. [b] Variations in temperature, solvent, concentration, rate of additions, and acetylating compounds will divert the addition to other than the desired positions.

give 28 g (85%) of **2**: mp 23.5–24 °C; NMR ($CDCl_3$) δ 2.22 (s, 3, CH_3), 5.14–5.38 (d, 2, $=CH_2$), and 7.14–8.60 ppm (m, 9, aromatic).

Synthesis of 9-Vinylanthracene (3). 9-Vinylanthracene was prepared by the Wittig reaction from 9-anthraldehyde. To a solution of 180 g of triphenylmethylphosphonium bromide (0.51 mol) in 800 ml of THF is added under nitrogen 190 ml of a 20% solution of *n*-butyllithium in hexane. One hour later a warm solution of 103 g of 9-anthraldehyde in 200 ml of THF is added dropwise and the mixture is refluxed 1 h. One liter of hexane is added, the precipitate is filtered, and after removal of solvent the product is purified by column chromatography on basic alumina (Woelm) to yield 50 g (45%) of **3**, mp 65 °C (lit. 64–65 °C[11]).

9-Vinyl-10-methylanthracene (4) was synthesized from 10-methyl-9-anthracene carboxaldehyde (Aldrich) using the Wittig procedure; 36 g (0.1 mol) of triphenylmethyl phosphonium bromide in 300 ml of dry THF was treated under nitrogen with a hexane solution of *n*-butyllithium (0.1 mol) and stirred for 2 h. A solution of 22 g of 10-methyl-9-anthracene carboxaldehyde in 100 ml of dry THF was added slowly and the mixture was refluxed for 2 h. One liter of hexane was added to the cold solution and the precipitate was filtered off. The filtrate was evaporated and the residue chromatographed on alumina (Woehlm neutral) to give 17 g (75%) of **4**. Recrystallization from hexane gave **4** as very pale yellow crystals: mp 112 °C; NMR ($CDCl_3$) δ 3.08 (s, 3, CH_3), 5.36–5.40, 5.65–5.69, 5.83–5.86, 6.03–6.03 (q, 2, $=CH_2$), 7.2–7.7 and 8.1–8.5 ppm (m, 9, $-CH=$ and aromatic).

Purification and Handling of Monomers. The recrystallized monomers were purified by column chromatography over basic alumina (Woelm) under oxygen free conditions. The eluent was evaporated and the monomers were stored in evacuated ampules in darkness. The purified monomers were not exposed to air prior to polymerization.

Polymerization and Characterization of Polymers. The polymerization techniques and the methods of polymer characterization were described in part 2.[2]

Results and Discussion

Although the synthesis of **3** via 1-(9-anthryl)ethanol is well known,[9] we found the Wittig procedure, direct conversion of 9-anthraldehyde to **3**, more reliable and easier. Both 1- and 2-vinylanthracene have been prepared via the corresponding anthryl ethanols but instead of the high-temperature dehydration of the alcohols we chose the much milder conversion to the chloride (by thionyl chloride) followed by the dehydrochlorination in the presence of a strong base (Li_2CO_3/DMF). Both are high yield, facile reactions.

The most difficult procedure in the synthesis of the 1- and 2-vinylanthracene monomers is the preparation of the specific acetylanthracene derivative. The procedures reported by Hawkins,[10] Etienne,[13] and Gore[11] are low-yield processes requiring tedious and difficult separation of the isomer mixtures. Also, minor variations in the reaction conditions can drastically affect the products and tend to make the acetylation reactions poorly reproducible.

We have found that the Friedel-Crafts acetylation can be directed to the 2-position (with no detectable amounts of 1- or 9-isomers) when the reaction is carried out in nitrobenzene with acetic anhydride as the acetylating agent and the ratio $AlCl_3$/acetic anhydride is maintained constant throughout the reaction. This is achieved by addition of the preformed $AlCl_3$/acetic anhydride complex to anthracene. Other variations of the addition sequence, e.g., $AlCl_3$ added to a mixture of anthracene/acetic anhydride, always led to lower and less reproducible yields. Similarly, the highest yields (over 60%) of 1-acetylanthracene (**5**) were obtained in methylene chloride with acetyl chloride at an approximately 2:1 mol ratio of $AlCl_3$ to acetyl chloride, when the preformed $AlCl_3/CH_3COCl$ complex was added slowly to anthracene. In this case we were not able to detect any 2-isomer and the only major by-product was 1,5-diacetylanthracene, which could be easily removed by recrystallization from benzene leaving **5** predominantly in solution. (**5**) then can be isolated by evaporation of the solvent and recrystallization from ethanol. The amount of 1,5-diacetylanthracene increases with increasing ratios of ($AlCl_3/CH_3COCl$) to anthracene. At low ratios, however, some anthracene remains unreacted and, since this is more difficult to separate, some trade-off is necessary. The acetylation reaction conditions giving the optimum yields of purified product for the 1-, 2-, and 9-acetylanthracene derivatives are summarized in Table I.

In parts 1 and 2 of this series[1,2] the extreme importance of monomer purity in the polymerization of 2-vinyl- and 2-propenyl-2-anthracene was emphasized. The exposure of the monomers to air can completely inhibit their anionic polymerization. In this present series of experiments we subjected the 1- and 9-substituted anthracene monomers to the same purification treatment prior to polymerization. The results were as follows.

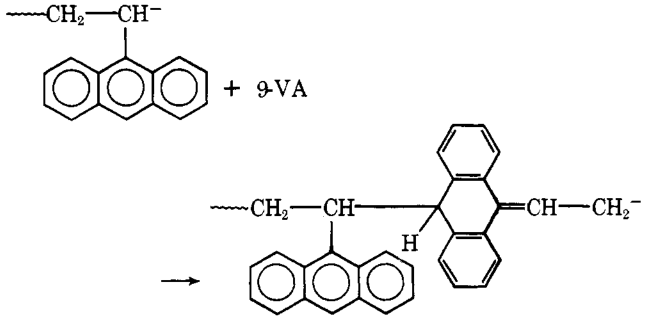
Radical Polymerization. 9-Vinylanthracene. Rigorous purification did not result in any improvements over the previously published art and only low yields of very low molecular weight products ($\overline{M}_n \gtrsim 10^3$, $\overline{DP} < 10$) could be isolated. Polymerization proceeded only in bulk; little or no polymer or oligomer was obtained in solution.

9-Vinyl-10-methylanthracene. Bulk polymerization carried out at 140 °C using *tert*-butyl peroxide as initiator (0.5–2 wt %) resulted in about 30% yield of low molecular weight polymer ($\overline{M}_n \approx 2\text{–}5 \times 10^3$) in 140 h.

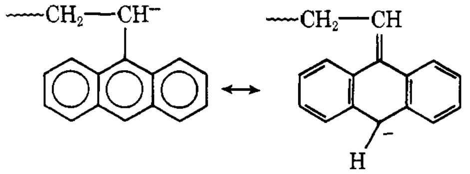
1-Vinylanthracene. High yields of low molecular weight (>70%) poly(1-VA) can be obtained by conventional free radical solution polymerization. For example, poly(1-VA) with $\overline{M}_n \approx 10^4$ was obtained in benzene at 55 °C using AIBN (1.0 wt % based on monomer) as initiator.

Anionic Polymerization. 9-Vinylanthracene. In spite of rigorous purification and careful handling of the monomer, no high molecular weight polymer could be obtained with any of the following initiators in THF or benzene over the temperature range −78 to +25 °C: sodium biphenyl, sodium naphthalene, butyllithium, α-methylstyrene tetramer dianion, and living polystyrene. No attempt was made to identify the structures of the oligomers that were produced in the reactions. The inactivity of 9-VA in anionic polymerizations is not related to any eventual impurity in the monomer but appears to be inherent to the structure. Spectroscopic analysis[14] of the polymerization of **3** reveals the immediate production of some species upon contact with either addition or electron transfer initiators that resemble the inactive species formed at elevated temperatures in the polymerization of 2VA and 2P2A.

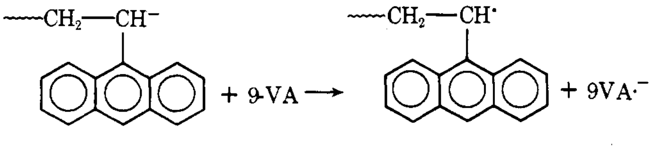
Several unsubstantiated mechanisms have been advanced to account for the anomalous ionic polymerization of 9-VA. Formation of stable "dormant" polymer anions can result from (a) a "wrong" type of monomer addition,[15]



or (b) isomerization of the growing polymer anion,



An electron transfer reaction from the polymer anion to the neutral monomer has also been proposed;



The free-radical species can undergo abstraction, combination, or disproportionation reactions to give dead polymer and the monomer radical anion can initiate further polymerization.[5]

9-Vinyl-10-methylanthracene. It was anticipated that blocking the reactive 10 position of the anthracene ring should greatly reduce the possibility for wrong monomer addition and isomerization. The electron transfer reaction is likely to be unaffected by the substitution. As with 9-VA, careful purification and handling of the monomer did not result in any increase in molecular weight of the polymer. The following initiators were utilized, sodium biphenyl, sodium naphthalene, butyllithium, α-methylstyrene tetramer dianion, and living polystyrene, with THF or benzene as solvent over the temperature range −78 to +25 °C.

Both 9-VA and 9V10MeA systems gave only low molecular weight polymer and in many of the reactions the polymer precipitated from the reaction medium. There has been no reported spectroscopic investigation of the anionic polymerization of 9-vinylanthracene which might elucidate the nature of the active species. Rembaum[5] studied the anionic polymerization in detail using dilatometric techniques and mentioned a green color in his studies. Michel[4] also reported the formation of a red followed by a green color in the reaction of sodium biphenyl and 9-VA in THF solution.

In order to try to define the nature of the propagating anion in the polymerization of 9-vinyl-10-methylanthracene we investigated the species formed in the reaction of $\sim S^-$, K^+ with monomer in THF at −70 °C. Mixing of the two solutions resulted in a slow (∼5–10 min) change from the red color characteristic of $\sim S^-$ to a green color (λ_{max} ∼620, 450 (sh), and 410 nm). The green solution was stable at room temperature (24 h) and assuming that all $\sim S^-$ was converted into the vinylanthracene anion, VA^-, the extinction coefficients were estimated to be 620 nm (10^4) and 410 nm (5×10^4). Quenching, isolation, and spectroscopic analysis of the polymer (essentially polystyrene) from the reaction revealed the presence of anthracene, indicating that some addition had taken place. A similar result was obtained in reaction at ambient temperature. With sodium biphenyl as initiator the green color resulted immediately on mixing the two solutions. All these reactions were carried out with a slight excess of monomer. When an actual polymerization reaction was attempted, i.e., a large excess of monomer, a brown colored solution was produced (λ_{max} ∼650, 560, and 455 nm) rather than the green solution reported earlier.

The polymerization of 9-vinyl-10-methylanthracene, like 9 vinylanthracene, results in low molecular weight polymer. The anionic system does not behave as a conventional addition polymerization and spectroscopic analysis of the propagating carbanion has been inconclusive. The absorption spectrum expected for the conventional propagating vinylanthracene carbanion $\sim CH_2-\bar{C}H(A)$ should be very similar to that of the analogous arylmethide anion, ACH_2^-, previously reported by us.[16] The species has absorption maxima in the visible at 715 nm, 675 nm with $\epsilon \sim 6 \times 10^3$ and 470 nm with $\epsilon \sim 1.2 \times 10^4$. A more detailed spectroscopic analysis of the anionic polymerization of the 1-, 2-, and 9-vinylanthracene series of monomers is presented in part 4 of this series.

1-Vinylanthracene. 1-VA can be polymerized by anionic addition type initiation to high molecular weight polymers. As in the case of 2-VA and 2P2A, the polymerization proceeds with highly purified (white) monomer that had not been exposed to air before polymerization. At low temperature (−78 °C) the yields are practically quantitative (Table II).

The polymerization reaction is effective at low temperatures, −60 to −80 °C. The active propagating species is very rapidly deactivated at higher temperatures and appears to be considerably more unstable than the carbanions from 2-VA and 2P2A. At temperatures above −50 °C low yields of low molecular weight polymers are produced. The 1-VA polymeric carbanion is green in color with long wavelength absorption bands in the 500–590 nm region. The solution changes to a brown color on warming and loses its polymerization capability.

The major advantage of 1-VA over the 2- and 9-vinylanthracenes is its higher solubility in many organic solvents. Essentially quantitative yields of polymer were obtained at −70 °C in 4–6 h. Molecular weights ($\overline{M}_n$) in the 10^4–10^5 range with molecular weight distributions close to 2 were achieved and the polymers were readily soluble.

Comparison of the ir spectra of the monomer (1) and the polymer (Figure 1) suggests a conventional vinyl structure with no involvement of the anthracene ring. This is similar to the 2-vinylanthracene polymers.

2-Propenyl-1-anthracene. This monomer could not be polymerized with either addition or electron transfer initiators in THF or benzene over a wide temperature range, −80 to +25 °C.

Cationic Polymerization. 9-Vinylanthracene. The monomer can be readily polymerized by conventional initiators such as $BF_3 \cdot OEt_2$ in CH_2Cl_2 and other solvents to give linear soluble polymers with $\overline{M}_w \approx 20\,000$. Although this is not significantly higher than the maximum reported value (∼8800),[4] it does indicate that the appropriate reaction conditions can give higher molecular weight, soluble polymers.

9-Vinyl-10-methylanthracene. The cationic polymerization of 9-vinyl-10-methylanthracene was attempted in a series of solvents (CH_2Cl_2; $CHCl_3$; benzene) using several initiators: $TiCl_4$, $BF_3 \cdot OEt_2$; tropylium hexafluoroborate, $SnCl_4$. As in the case of 9-VA, only low molecular weight soluble polymers ($\overline{M}_n = 10^3$–10^4) were obtained.

1-Vinylanthracene, 2-Propenyl-1-anthracene. Both 1-VA and 2P1A failed to polymerize cationically under a variety of conditions.

Polymer Structure. The polymers of 1-vinylanthracene

Table II
Anionic Polymerization of 1-VA

1-VA, g	Solvent	Initiator [LE]; mol × 10^5	T, °C	Time, h	Yield, %	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
2.0	THF	$\sim S^- Na^+$; 6.6	−70	5	~100	78 000	2.4
3.0	THF	Cumyl potassium; 6	−60 to −70	5	~100	79 000	1.8

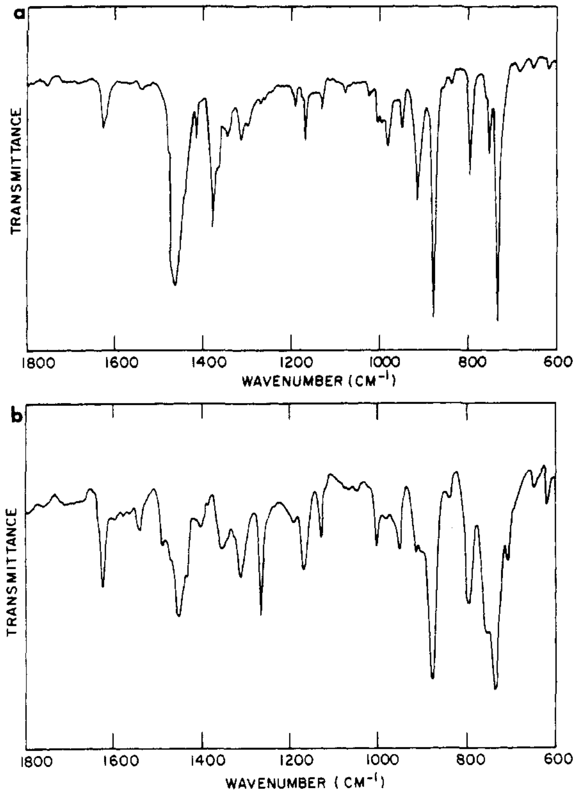
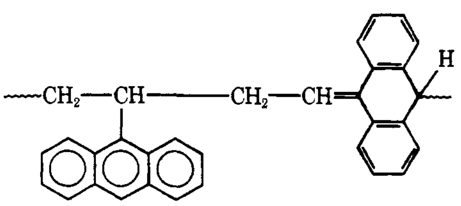


Figure 1. Infrared spectrum of: (a) 1-VA (in Nujol); (b) poly(1-VA) film.

synthesized during this investigation and the 2-vinylanthracene polymers reported in part 2 possess conventional vinyl structures. There is no evidence from solubility or spectroscopic studies to support any significant involvement of the anthracene moiety in the propagation step. Such a reaction has been invoked in the polymerization of 9-vinylanthracene to accommodate some unusual solubility and spectroscopic results on the polymers, e.g.,



From a study of the ir and uv spectra of the low molecular weight ($\overline{DP} < 20$) polymers formed in the anionic and cationic polymerization of 9-VA, both Michel[4] and Rembaum[5] concluded that the materials contained significant amounts of the 1,6 structure. The evidence for this was (1) the existence of a band at 13.2 μm in the ir which is not characteristic of substituted anthracenes (13.7 μm) and (2) anomalous extinction coefficients for the absorption bands at ~370 and ~260 nm in the polymers compared to some anthracene model compounds. The spectral data were more consistent with the 9,10-dihydroanthracene ring type structure.

Further support for this structure came from the NMR spectra of the polymers. Michel[4] attributed the absence of conventional vinyl hydrogen absorption peaks above τ 7.5 and the appearance of a vinylic absorption at τ 4 to the postulated 1,6 structure. Also, bands at τ 6 and 7.3 were assigned to the dihydroanthracene hydrogen and the allylic hydrogen, respectively.

Further indirect evidence favoring the anomalous ring type structure came from: (1) reaction of the polymer with maleic anhydride indicating ~30% conventional anthracene groups,[5] (2) properties of the polymeric complexes[5], e.g., with I_2, (3) stability of the polymer polyradical anions,[5] and (4) conversion of the polymer to poly(9,10-dimethyleneanthracene) by treatment with CF_3COOH in CH_2Cl_2 (this latter polymer prepared independently is known to be extremely insoluble).[4]

The ionic polymerization of 9-VA characteristically results in both soluble and insoluble products reputed to contain both the 1,2 and 1,6 structural units. Marechal[6] showed that in the cationic case, polymerization at low temperature (< − 70 °C) produced essentially pure 1,6 polymer and the amount of 1,2 polymer increased with increasing temperature, with essentially pure 1,2 polymer being formed above 20 °C. Marechal also determined that the 1-VA, 2-VA, and 9-vinyl-10-methylanthracene polymers prepared by cationic initiation were conventional 1,2 polymers.

The ir and uv spectra of the polymers of the 1-vinyl-, 2-vinyl-, and 9-vinylanthracene monomers prepared in this study (this work and ref 2) are indicative of a conventional 1,2-vinyl structure. The NMR spectra of the high molecular weight polymers of 1- and 2-vinylanthracenes are broad and structureless and are characteristic of vinyl aromatic and heterocyclic polymers possessing bulky pendant groups;[14,18,20] i.e., they exhibit shifts in the absorption of the backbone hydrogens as well as an unusual upfield shift of some aromatic hydrogens. These shifts have been interpreted in terms of the steric constraints present in such polymers resulting in significant anisotropic magnetic shielding effects. The polymers exhibit broad aromatic absorption regions, τ 1.5 to 5. The NMR spectra of the poly(9-vinylanthracenes) synthesized in this study are similar to that published by Michel.[4] We propose that the NMR spectra of these low molecular weight polymers are also consistent with a conventional vinyl aromatic polymer structure and it is not necessary to invoke the anomalous 1,6 structure.

The anomalous spectroscopic data reported for poly(9-vinylanthracene) can also be explained by the facile dimerization process involving the pendant anthracene groups. The susceptibility of vinylanthracene polymers to air/light has been clearly established in the 2-vinylanthracene series. There is no evidence in the published literature on 9-vinylanthracene to suggest that the polymers (oligomers) were screened from O_2/uv prior to or during characterization. Furthermore, the low molecular weights of the polymers might require high levels of dimerization to achieve measurable changes in solubility characteristics. The anthracene dimerization reaction introduces dihydroanthracene functions into the polymers and these can account for the published ir, uv, and NMR spectral data. The vinylanthracene polymers synthesized in this study develop the spectral characteristics of oxidized and 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

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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