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Polymerization of Vinylanthracene Monomers. 2. 2-Vinylanthracene and 2-Propenyl-2-anthracene

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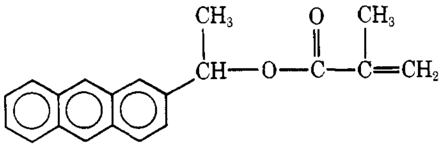
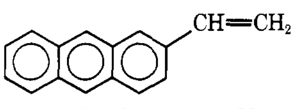
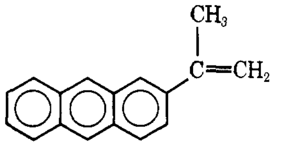
ABSTRACT: The synthesis of 2-vinylanthracene and 2-propenyl-2-anthracene and their polymerizations by free radical, anionic, cationic, and Ziegler techniques have been investigated. 2-Vinylanthracene and 2-propenyl-2-anthracene have been polymerized to high molecular weight polymers ($\overline{M}_n > 10^5$) by anionic addition type initiators. The polymerization reaction must be carried out with high purity monomer at low temperature (<-40 °C) to maximize molecular weight. Poly-2-vinylanthracene and poly-2-propenyl-2-anthracene are linear, soluble polymers with conventional vinyl structures. Both polymers undergo facile cross-linking and insolubilization in air/light. The cross-linking appears to result both from oxidation leading to free radicals and photodimerization of anthracene groups.

Until recently[1] *no high molecular weight polymers of* vinylanthracene were known. It was believed that the synthesis of such polymers by simple addition polymerization was not possible. This conclusion was based on several generally accepted facts: (1) anthracene is an efficient radical quencher and inhibits radical polymerization of vinyl monomers, including styrene, (2) anthracene inhibits or severely retards the ionic polymerization of vinyl monomers, (3) 9-vinylanthracene could not be polymerized to a high molecular weight polymer by any known technique.[2] It was concluded that the inability to prepare high molecular weight poly-9-vinylanthracene was inherently associated with the anthracene ring structure and, therefore, no real attempts were made to investigate other anthracene monomers. Katz[3] and Hawkins[4] reported the syntheses of 1- and 2-vinylanthracenes but were only able to obtain oligomers by standard polymerization techniques. It has recently been shown[5] that under certain conditions the anthracene containing monomer, 1-(2-anthryl)ethylmethacrylate, can be polymerized to a conventional high molecular weight vinyl type polymer by free-radical methods. During investigations of this anthryl methacrylate polymerization it was established that monomer purity is extremely important in attaining high molecular weight products. In view of this finding it was decided to re-examine the polymerization of 2-vinylanthracene and its α-methyl analogue, 2-propenyl-2-anthracene;





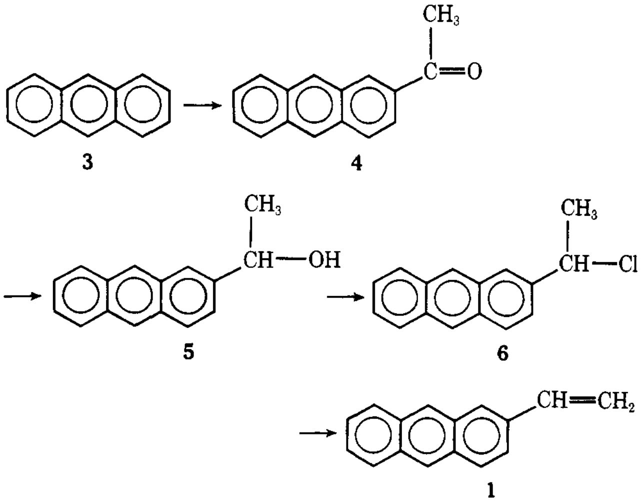
2-vinylanthracene (2-VA)
1



2-propenyl-2-anthracene (2P2A)
2

Experimental Section

Synthesis of 2-Vinylanthracene. 2-Vinylanthracene (2-VA) (1) was synthesized from anthracene by the following reaction scheme which is a modification of the procedure of Etienne et al.[6]



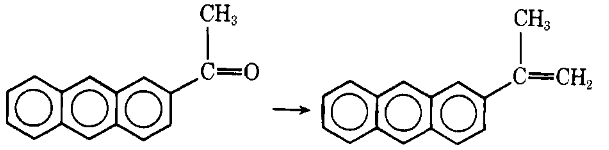
2-Acetylanthracene (4). In a 3-l. flask 150 g (0.84 mol) of anthracene (**3**) is dispersed in 150 ml of nitrobenzene. The dispersion is cooled to 15 °C. In a separate vessel, 255 g (1.9 mol) of $AlCl_3$ is dissolved in 480 ml of nitrobenzene. To this solution (cooled to room temperature) is slowly added 155 ml (1.6 mol) of acetic anhydride. The complex $AlCl_3$/acetic anhydride is cooled and slowly (over at least 1 h period) added to the vigorously stirred anthracene suspension. The reaction mixture is maintained at 15 °C for an additional 16 h. The red complex of the product is precipitated by addition of 1500 ml of cold benzene. The solid is filtered and washed with about 200 ml of cold benzene and then with hexane. It is essential at this step to remove as much nitrobenzene from the red complex as possible. The red complex is then hydrolyzed in ice–HCl (2 l. of broken ice/200 ml of concentrated HCl) and the greenish product is filtered, washed with water, dried, and recrystallized from benzene/hexane after treatment with activated charcoal to give 98 g (50%) of light yellow-green crystalline product, mp 188 °C (lit. 186–188 °C;[6] 186–187 °C;[7] 190–192 °C;[4] 188 °C[8]).

1-(2-Anthryl)ethanol (5). Sodium borohydride ($NaBH_4$) (25 g, 0.53 mol) in 280 ml of H_2O is slowly added to a refluxing suspension of 53 g (0.24 mol) of 2-acetylanthracene in 1800 ml of ethanol. The yellow solid dissolves upon addition of about two thirds of the borohydride and the solution turns gold-brown. After 2 h refluxing about 1 l. of the solvent is distilled off, the product is precipitated with water, washed with dilute HCl and water, dried, and recrystallized (following charcoal treatment) from benzene to give 40 g (75%) of white crystalline product, mp 164 °C (lit. 162–163 °C;[6] 156–157 °C;[3a] 162–163 °C[7]).

1-Chloro-1-(2-anthryl)ethane (6). Thionyl chloride ($SOCl_2$) (20 ml) is slowly added to a refluxing solution of 39 g of **5** in 500 ml of benzene. The solution is refluxed for 2 h; then, about 250 ml of benzene is distilled off; the residual slurry is cooled and poured into an excess of petroleum ether (about 1.2 l.). The precipitated solid is washed, dried, and recrystallized from benzene/hexane to give 35 g (83%) of light green powder, mp 170–178 °C dec.

2-Vinylanthracene (1). 1-Chloro-1-(2-anthryl)ethane (**6**) (33 g) is dehydrochlorinated in 300 ml of dimethylformamide containing 20 g of Li_2CO_3 at 130 °C. After 4 h the mixture is cooled and **1** is isolated by precipitation with water. Two recrystallizations from benzene/methanol (with charcoal treatment) yield 20 g (60%) of light yellow powder, mp 205–210 °C. Further purification by column chromatography from alumina using nitrogen-purged solvents and eluents yields white crystalline product: mp 211 °C (lit. 210–211 °C;[6] 186–187 °C;[3a] 186.5–188 °C[4]); NMR ($CDCl_3$) δ 5.25–5.44, 5.71–6.00 (d, 2, $=CH_2$), 6.67, 6.85, 6.97, 7.14 (q, 1, $-CH=$), and 7.32–8.35 ppm (m, 9, aromatic).

Synthesis of 2-Propenyl-2-anthracene (2). This monomer was prepared by Wittig reaction from 2-acetylanthracene:



50 ml of *n*-butyllithium solution (2.2 mol/l. of hexane) is introduced into a flask containing 36 g of triphenylmethylphosphonium bromide (0.1 mol) and 200 ml of tetrahydrofuran at 0 °C in N_2 atmosphere. The combined solution is stirred at 0 °C for 1.0 h under nitrogen. 2-Acetylanthracene (22 g) dispersed in 500 ml of tetrahydrofuran is added to the above solution and the mixture is refluxed for 60 min. The solids are filtered off. From the liquid portion, approximately 600 ml of THF is evaporated, and the remainder is poured into a mixture of 500 ml of H_2O and 500 ml of EtOH. The yellow precipitate is filtered, washed, dried, and purified by chromatography from the basic alumina (Woelm) using benzene as eluent. The product is a white crystalline material: mp 152–153 °C (lit. 154 °C[9]); NMR ($CDCl_3$) δ 2.21 (s, 3, CH_3), 4.95–5.35 (d, 2, $=CH_2$), and 6.83–7.94 ppm (m, 9, aromatic).

Polymerization Procedures. The recrystallized monomer was purified by column chromatography (Woelm basic alumina) under oxygen free conditions and in dim lighting. The monomer/eluent solutions were collected in ampules and the solvent was removed under high vacuum. Ampules were stored in a refrigerator in the dark. Polymerization reactions were carried out using standard experimental techniques with vacuum or nitrogen manipulation of the solvents, monomers, and initiators. Polymerization reactions were run in the dark to eliminate any photoinduced complications and the product polymers, after precipitation with a nonsolvent, were handled as far as possible in oxygen free conditions under dim lighting.

Polymer Characterization. Both poly-2-vinylanthracene and poly-2-propenyl-2-anthracene were readily soluble in a number of organic solvents, e.g., $CHCl_3$, THF, toluene, etc. The polymers were found to undergo facile cross-linking and insolubilization in the presence of air and light. This made characterization extremely difficult and necessitated the use of degassed solutions and handling of solutions under appropriate lighting conditions. Poly-2-propenyl-2-anthracene was more stable toward cross-linking and was used for most of the analytical determinations.

$\overline{M}_n$ and $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ values were measured by GPC and membrane osmometry. The measurements were reproducible provided reasonable handling precautions were taken and fresh solutions were used. $\overline{M}_n$ values were estimated using a Hewlett-Packard 502 high speed membrane osmometer with THF as solvent. A Waters Model 200 gel permeation chromatograph was employed to measure the molecular weight distribution, $\overline{M}_w/\overline{M}_n$. The instrument was calibrated for THF as solvent with standard polystyrenes (Pressure Chemical). Both poly-2-vinylanthracene and poly(2-propenyl-2-anthracene) exhibit solution properties characteristic of a number of vinyl aromatic polymers and can be accommodated on the universal GPC calibration curve for such polymers.[10]

Optical spectra were recorded on a Cary 14 spectrophotometer, ir spectra on a Perkin-Elmer 267 spectrometer, and NMR spectra on a Jeolco C-60H spectrometer. Both solution and thin film ir spectra were measured.

Results and Discussion

The problems associated with the radical and ionic polymerization of 9-vinylanthracene (9-VA) have been discussed in a review by Rembaum and Eisenberg[2] and in several other studies.[3,11–13] The polymerization is characterized by anomalous kinetics, low reaction rates, low molecular weights, and ill-defined structures of the products. Several mechanisms have been proposed to explain the experimental observations in the anionic polymerization of 9-VA.[2,14] However, no clear unambiguous experiments have been reported which would clarify the mechanism.

We have noted some differences in the chemical behavior of 9- and 2-substituted anthracenes, e.g., in Diels-Alder reactions with maleic anhydride and diethyl azodicarboxylate. While anthracene and its 9-substituted derivatives react spontaneously in quantitative yields, the corresponding 2-isomers react sluggishly or not at all. These differences and particularly the success in polymerizing the methacrylate of 2-substituted anthracene[5] have led us to reinvestigate in more detail the polymerization of 2-vinylanthracene monomers. 2-Vinylanthracene, 2-VA, is known[3,4] but the synthesis is difficult and low in yield. We have succeeded in optimizing the procedures, particularly the acetylation reaction, to produce the 2-acetylanthracene intermediate. The synthesis of 2-propenyl-2-anthracene has also been reported[4] but the Wittig reaction on 2-acetylanthracene turned out to be a more straightforward and much easier reaction than the reported synthesis.

Free-Radical Polymerization. 2-VA can be readily polymerized in solution (Table I). The polymerization in bulk or emulsion is not feasible due to the high melting point of the monomer (211 °C). The solubility of 2-VA in common organic solvents is extremely low and temperatures above 100 °C are required to achieve a monomer concentration which gives reasonable polymerization rates and molecular weights. Chain transfer processes became favored at elevated temperatures but this trade-off is apparently inevitable. In xylene at 115 °C the transfer reaction with the solvent is probably significant, but the molecular weights are relatively high considering the published data for 9-VA. Tributyl phosphate, which is reported to be low transfer medium for styrene polymerization, is a good solvent for the monomer but is a precipitant for the polymer and cross-linked products were obtained.

All attempts to polymerize 2P2A by radical initiation were unsuccessful, very likely due to a ceiling temperature effect as in the case of α-methylstyrene and related α-substituted vinyl monomers.

Table I
Free-Radical Polymerization of 2-VA

2-VA, g	Solvent, ml	Initiator[a]	T, °C	Time, h	Yield, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1.0	Tributyl phosphate, 4	TBP	115	72	100		Insoluble	
1.0	Xylene, 10	TBP	115	72	100	13 200	60 000	4.5
1.0	Tributyl phosphate, 6	TBP	80	24	2		Insoluble	
1.0	Tributyl phosphate, 10	TBP	135	5	100		Insoluble	
1.0	Toluene, 10	TBPI	80	24	100	10 000	29 500	2.9

[a] TBP = di-*tert*-butyl peroxide, 1 wt %. TBPI = *tert*-butyl peroxyisobutyrate, 1 wt %.

Table II
Anionic and Ziegler-Type Polymerization of 2-VA

2-VA, g	Solvent	Initiator [LE]; mol × 10^4	T, °C	Time, h	Yield, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
5.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 1.0	−60 up to −10	24	60	22 100	35 500	1.6
10.2	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 10	−50	1	0.2	16 000	29 500	1.8
3.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 0.5	−78	100	60	318 000	910 000	2.9
5.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 2.0	−78	150	100	160 000	830 000	5.2
5.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 2.0	−30	120	100	290 000	2 950 000	10.1
3.8	Benzene	$AlEt_3 + TiCl_4$; 2.1	25	48	82		Insoluble	

Table III
Anionic and Ziegler-Natta Polymerization of 2-Propenyl-2-Anthracene

2P2A, g	Solvent	Initiator [LE]; mol × 10^4	T, °C	Time, h	Yield, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
3.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 2.0	−78 to −50	6	90	34 000	48 000	1.4
9.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 1.6	−78	24	100	172 000	300 000	1.7
9.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 1.6	−30	18	100	170 000	300 000	1.7
5.0	C_6H_6	BuLi; 0.15	25	48	<10		Oligomers	
14.0	THF	$\alpha MeS_4{}^{2-}$, $2Na^+$; 0.8	−30	72	80	216 000	470 000	2.2
3.8	C_6H_6	$AlEt_3$-$TiCl_4$; 2:1	25	48	30	15 500	26 500	1.7

Anionic Polymerization. Anionic polymerization of both 2-VA and 2P2A can be initiated with addition type initiators such as living polystyrene and the α-methylstyrene tetramer dianion, $\alpha MeS_4{}^{2-}$. Some typical results are presented in Tables II and III. Attempts to initiate polymerization with electron transfer type initiators, e.g., sodium naphthalene and sodium biphenyl, were unsuccessful, resulting in poor yields and oligomeric products.

The polymerization reactions are effective at temperatures below −40 to −50 °C and the optimum results were obtained at −78 °C. With increasing temperature both the yield and the molecular weight of the polymers tend to decrease and the molecular weight distribution increases. Polymerization at temperatures above −20 °C gave essentially no polymer products.

The extremely low solubility of 2-VA in typical solvents for anionic polymerization at −78 °C results in extremely low polymerization rates. The reaction proceeds in a heterogeneous system with the soluble portion of the monomer, which is consumed in the polymerization, being replenished from the nondissolved particles. Since both the polymeric carbanions and the polymer are completely soluble, the disappearance of the solid monomer particles is a measure of the conversion. For both 2-VA and 2P2A the polymeric anions are purple in color with long wavelength absorption bands in the 500–560 nm region. Increasing the temperature results in spectral changes and a decrease in polymerization activity. The detailed spectroscopic and mechanistic issues of the 2-vinylanthracenes and other vinylanthracenes will be covered in part 4 of this series.

The results in Tables II and III indicate that high yields of high molecular weight polymer can be obtained by polymerization at low temperature for periods of days. Unlike the more classical anionic polymerizations, molecular weight distributions considerably greater than 1 were realized. In view of the long reaction times and the unusual heterogeneous nature of the polymerizations, molecular weight distributions >2 are not unexpected. The unstable nature of the propagating polymeric carbanions at elevated temperatures is also consistent with these broad molecular weight distributions.

2P2A is more soluble than 2-VA and the increased solubility is reflected in higher reaction rates, 80 to 100% conversion in 1–3 days at −30 to −78 °C, and somewhat narrower M_w/M_n values. In both systems there is a rough correlation between molecular weight and (M)/(LE), but in general it is difficult to exercise a high degree of control over the product molecular weights.

The feasibility of synthesizing block copolymers was demonstrated by polymerizations of 2-VA and 2P2A initiated by living polystyrene. The spectrum of living polystyrene changed immediately to that of living poly(2-VA) or poly(2P2A) when these monomers were added. Similarly, a block copolymer of 2-vinyl-*N*-ethyl carbazole and 2P2A was obtained when the living poly(2-vinyl-*N*-ethylcarbazole) was used as initiator. The reverse sequence was also demonstrated; i.e., $\sim\sim$2P2A$^-$ initiates the polymerization of styrene. Some typical results are shown in Table IV. The block copolymer nature of the products was established by chemical analysis, solubility, and GPC characterization. In view of the complexities associated with the anionic polymerization of the 2-vinylanthracene monomers these block copolymer systems were not pursued any further.

It should be stressed that the monomer purity requirements in these systems are extremely high. In addition to impurities which should be avoided in common anionic polymerizations such as water or other spurious terminating species, these polymerizations appear to be very sensitive to oxidation products of anthracene compounds. Both monomers are

Table IV
Block Copolymerization of 2-Propenyl-2-Anthracene

Initiator	Monomer 1 g, time	Monomer 2 g, time	Solvent	Temp, °C	Yield, g	Composition M1:M2
Cumyl$^-$, K$^+$	N-Et-2VK[a] 2.0, 15 min	2P2A 2.0, 18 h	THF	−40	4.0	50:50
Cumyl$^-$, K$^+$	Styrene 1.0	2P2A 0.5, 24 h	THF	−40	1.5	33:67

[a] *N*-Ethyl-2-vinylcarbazole.

Table V
Cationic Polymerization of 2-VA

2-VA, g	Solvent	Initiator; mol × 10^5	*T*, °C	Time, h	Yield, %	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1.0	CH_2Cl_2	BF_3·OEt_2; 5	25	45	80	7000	10 500	1.5
1.0	CH_2Cl_2	BF_3·OEt_2; 5	−78 to 25	72	70	6900	10 700	1.6
1.0	CH_2Cl_2	BF_3·OEt_2; 1	30	48	60	8900	17 200	1.9
3.0[a]	CH_2Cl_2	BF_3·OEt_2; 1	25	48	0			
5.0[a]	CH_2Cl_2	Tropylium hexafluoroborate; 2	−30 raised to 25	72	0			
5.0[a]	CH_2Cl_2	BF_3·OEt_2; 2	−30	48	0			
			25	100	0			

[a] Very pure monomer; recrystallization followed by chromatographic purification.

readily oxidized in air, particularly in light, and, therefore, must be handled in the absence of oxygen under subdued lighting.

Polymerization with Ziegler Catalyst. 2-VA was polymerized in the presence of the $AlEt_3$–$TiCl_4$ catalyst under conditions in which styrene yields an isotactic polymer.[15] The yield of polymer was moderate. The polymer was, however, insoluble and the x-ray analysis showed the polymer is completely amorphous. On the other hand, the Ziegler-type catalyst ($AlEt_3$–$TiCl_4$) initiated polymerization of 2P2A and produced a soluble polymer. We were not able to detect any steroregularity in poly(2P2A). The x-ray analysis showed no crystalline patterns even in annealed samples. The infrared spectra of the anionically polymerized 2P2A and that of the Ziegler-type polymerization were identical.

Cationic Polymerizations. Highly purified 2-VA and 2P2A (purity required for successful anionic polymerization) did not polymerize cationically in the presence of BF_3·OEt_2, tropylium hexafluoroborate, or $TiCl_4$ in CH_2Cl_2 at temperatures ranging from −78 to +25 °C. However, 2-VA purified only be repeated crystallization (mp 210 °C) could be polymerized in methylene chloride using the BF_3·OEt_2 catalyst (Table V). Apparently some cocatalytic species that is present in "crude" 2-VA in typical solvents used for cationic polymerization made it impossible to run the reactions under optimum conditions. In order to achieve reasonable reaction rates and yields, the polymerizations had to be carried out at elevated temperatures (25–35 °C). The molecular weights of the products were low, probably as a result of excessive chain transfer under those conditions. The highest molecular weight of P2VA achieved was M_w = 17 200.

Structure of Poly(2-VA) and Poly(2P2A). Infrared, uv, and NMR analysis revealed no detectable difference between the structures of the radical and ionic polymers. In all cases, except in the Ziegler-type polymerization of 2-VA, completely soluble polymers were obtained. The ir spectra of the monomers and the polymers are compared in Figures 1 and 2. The spectra are virtually identical with the exception of the vinyl band and are indicative of a conventional linear vinyl type structure. There is no evidence to support any major involvement of the anthracene ring in the propagation step. This conclusion is further supported by the uv spectra of the polymers which are characteristic of 2-substituted anthracenes.

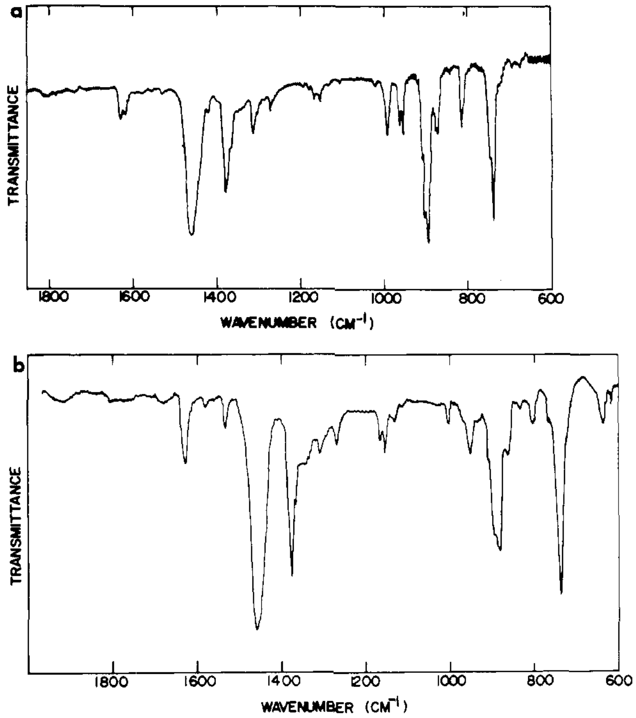


Figure 1. Infrared spectrum of: (a) 2-VA (in Nujol); (b) P(2-VA) (film).

The NMR spectra of the polymers are shown in Figures 3 and 4. The spectra exhibit poor resolution and are typical of high molecular weight vinyl polymers. The peaks are broad and there is very little detailed structural information which can be realized. The very broad aromatic proton absorption band, from τ 1 to 5, is indicative of appreciable degrees of shielding arising from interring interactions in the polymers. Similar phenomena have been reported for other vinylaromatic/vinylheterocyclic polymers possessing bulky pendant groups, e.g., vinylcarbazoles, vinylpyrene, and vinylacridine.[16–18]

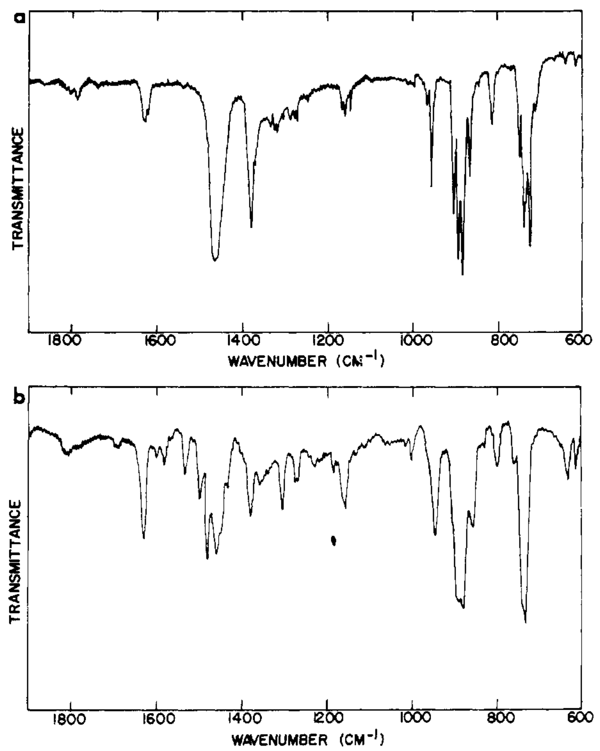
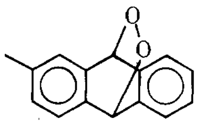


Figure 2. Infrared spectrum of: (a) 2P2A (in Nujol); (b) P(2P2A) (film).

All the polymer samples, including the Ziegler–Natta polymers, are amorphous. No crystallinity was detected even after annealing at various temperatures.[19] The T_g of high molecular weight poly(2-VA) is in the region of 175 °C.

Both polymers, and particularly poly(2-VA), are very easily cross-linked in air, both in the solid state and in solution. Short exposure to air, especially in light (minutes or hours), causes insolubilization of the polymers or gelation of the polymer solutions. The facile cross-linking probably results from oxidation of anthracene to the peroxide



followed by thermal or photoactivated decomposition of the peroxide to produce radicals. Cross-linking can also result from the photodimerization of anthracene rings in the polymer. This process is accompanied by the disappearance of the spectral absorption bands characteristic of anthracene. The reaction product is a 9,10-dihydroanthracene dimer which has no absorption in the 350–450 nm region. This reaction can be intra- or intermolecular, depending on the environment.

The strong tendency of the polymers to oxidize and cross-link made investigation of the physical properties extremely difficult. However, both polymers are reasonably stable if stored in darkness and at low temperatures. It is advisable to store poly(2-VA) in solution; the solid poly(2-VA) became insoluble after about a 3-month period in the refrigerator.

The achievement of high molecular weight polymers of 2VA and 2P2A using anionic polymerization techniques demonstrates that under suitable conditions the complicating transfer and termination reactions reported for 9-vinylanthracene are not significant in these systems. The fact that the polymers possess conventional linear vinyl structures is also strong evidence for normal propagation. In the case of the free radical and cationic polymerization systems, the low molecular weights attained reflect the unfavorable nature of the polymerization system. It has not been possible to locate a solvent with the appropriate combination of properties (e.g., monomer solubility, polymer solubility, low chain transfer constant, low freezing point, etc.) to permit reaction under the most favorable conditions.

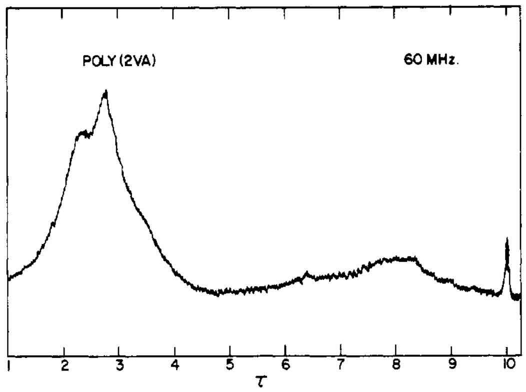


Figure 3. NMR spectrum of P(2-VA).

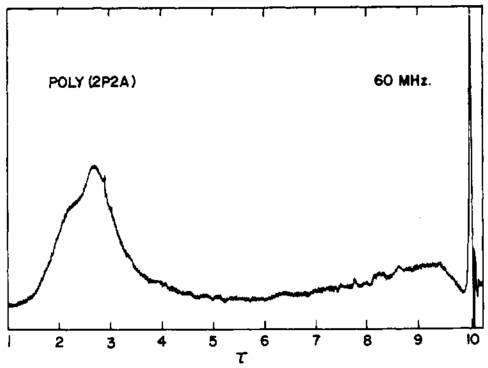


Figure 4. NMR spectrum of P(2P2A).

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