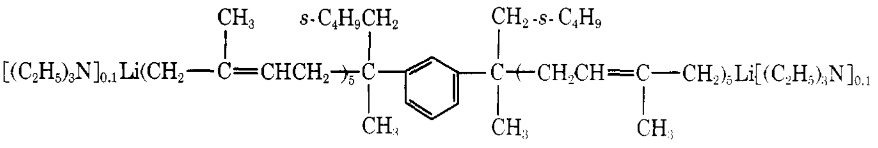

I

of the salts to polymerize pivalolactone was done as described above.

Difunctional initiators used include DiLi-3,[5] which was obtained from the Lithium Corporation of America, and a new product we have made designated as Diplit 5.1 (I). DiLi-3 is made by addition of *sec*-butyllithium to divinylbenzene in the presence of triethylamine and has a functionality slightly over 2. We have made Diplit 5.1 (I) by addition of *sec*-butyllithium to *m*-diisopropenylbenzene in the presence of 0.1 equiv of triethylamine followed by addition of 5 equiv of isoprene. I is, within experimental accuracy, bifunctional.

ABA triblock copolymers containing 35–45% of pivalolactone were made from polyisoprenes of $M_n \sim 40\,000$ prepared using DiLi-3. Films pressed from these polymers at 215 °C and higher were tough and elastic. Strips cut from these films could be cold drawn when subjected to stress and became stronger and more elastic. When stretched and then relaxed and stretched again through a number of cycles, they became oriented and increased greatly in strength. Examples of properties of oriented films are given in Table I. Fibers melt spun at 215 °C and hand drawn were also strong and very elastic. A triblock copolymer containing 42% PVL had a tenacity (breaking stress) of 0.63 g/d[7] and an elongation at break of 430%.

Block-graft copolymers were made from polyisoprenes prepared using Diplit 5.1 as the initiator. These were compositions containing 15–50% PVL distributed as 5–18 segments per isoprene chain, with each segment having a DP of 12–90. The segments were attached to polyisoprene backbones of $\bar{M}_n$ = 35 000–90 000. The polymers could be melt-spun into fibers at 240–280 °C, which, after orientation by hand drawing, had tenacities as high as 1–1.5 g/d with elongations at break of 150–450%. Highest strengths were obtained with compositions having 35% PVL and higher. Typical values are given in Table II.

Table I
Properties of Pivalolactone–Isoprene ABA Triblock Copolymers

PVL		Tensile strength, MPa[6]	Elongation at break, %
Wt %	DP		
34	103	24.15	765
39	111	34.5	485
44	121	52.23	285

Table II
Properties of Block–Graft Copolymers

PVL Wt %	Polyisoprene $\bar{M}_n$	PVL segments		T_B, g/d	Elongation at break, %
		No.	DP		
25	60 000	4	60	0.4	660
35	53 000	4.8	60	0.6	400
35	52 000	6.1	46	0.9	480
35	75 000	11	37	0.9	450
35	92 000	11	47	0.9	430
40	57 000	6.6	57	1.0	440
41	60 000	18	32	0.8	300
49	67 000	13	48	1.68	160
50	59 000	6.5	90	0.85	210
51	60 000	18	49	1.38	170

Fibers protected against oxidation with phenyl-β-napthylamine were examined for cross-link stability by a long-term stress-decay test. This involved keeping the fiber extended 300% and noting decrease in stress with time. In 20 h, stress dropped about 20%. Since this decrease was the same as obtained with a control of sulfur-cured gum natural rubber, it can be inferred that the crystalline cross-links are comparable in stability to chemical cross-links.

A more detailed account will be published later.

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(6) 1000 psi = 6.90 MPa.

(7) Stress and moduli of fibers are customarily expressed in grams per denier (g/d). Denier is the weight in grams of 9000 m of the fiber.

(8) Contribution No. 2304.

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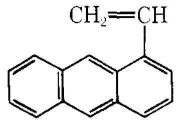
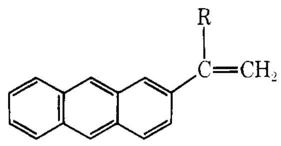
1. Polymerization of Vinylanthracene Monomers

The polymerization of 9-vinylanthracene has been studied by a number of authors[1-5] and a review article has been published[6] on this unique monomer. The 1- and 2-vinylanthracenes are also known but there has been very little published on their polymerization characteristics.[3,5,7] One universal conclusion that can be drawn from all these investigations is that high molecular weight, soluble polyvinylanthracenes cannot be synthesized by standard free radical or ionic polymerization procedures.

From a review of the above publications, the maximum degree of polymerization (dp) achieved in the polymerization of 1- and 2-vinylanthracene has been in the range of 5–20. The polymers were reported to possess the conventional 1,2 structures. In the case of 9-vinylanthracene, higher molecular weights have been claimed, dp ~ 25–35, but the polymers were reported to be mixtures of both 1,2 and 1,6 structural units:



1

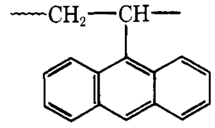


2, R = H
3, R = CH_3

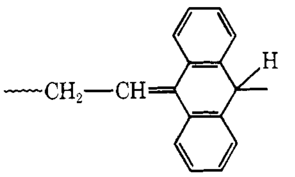
The intrinsic problems associated with achieving high molecular weight products from free radical and ionic polymerization of vinylanthracene monomers appear to be: (a) the high reactivity of the anthracene moiety toward free radicals resulting in chain transfer and chain termination; (b) the high electron affinity and reactivity of the anthracene moiety toward anions resulting in effective chain transfer, electron transfer, and termination processes; (c) the facile rearrangement of the carbanions and carbonium ions from the monomer resulting in chain transfer and termination reactions.

The assumption that the anthracene moiety is very reactive toward free radicals is not generally valid. It has been demonstrated[8] that 1-(2-anthryl)ethyl methacrylate can be polymerized by free radical initiators to high molecular weight polymers.

As part of our program on the synthesis and polymerization of vinyl aromatic[9] and heterocyclic[10] monomers, we have investigated a series of vinylanthracene monomers. In this preliminary communication we report the successful ionic polymerization of 1-vinylanthracene (1), 2-vinylanthracene (2) and 2-propenyl-2-anthracene (3) to high molecular weight, $\bar{M}_n = 10^5$–10^6, completely soluble polymers with conventional vinyl structures.



1, 2



1, 6

The most critical aspect of the polymerization of **1**, **2**, and **3** was the achievement of high purity monomer. Also, the polymer products were found to be extremely sensitive to oxidation and photochemical cross-linking, and analytical measurements (spectroscopic and molecular weight) had to be performed under appropriate lighting conditions with carefully prepared nitrogen purged solutions. Polymerization reactions were carried out using standard techniques and molecular weights were determined using membrane osmometry and GPC.

Polymerization of 2-Vinylanthracene Monomers. 2-Vinylanthracene (**2**) is readily polymerized in solution by free radical (peroxide) initiators. Because of its high melting point, 210 °C, bulk polymerizations were not feasible. The very low solubility of **2** necessitated the use of high temperatures, >100 °C, to attain reasonable monomer concentrations, reaction rates, and molecular weights. With xylene as solvent and di-*tert*-butyl peroxide as initiator complete conversion to polymer was attained in under 24 h at 115 °C. Polymers having $\bar{M}_n \sim 1.3 \times 10^4$ and $\bar{M}_w \sim 3.8 \times 10^4$, which were readily and totally soluble (e.g., benzene, THF, $CHCl_3$, etc.), were obtained. A good solvent for both monomer and polymer, which possesses a low chain transfer constant, has not yet been determined and higher molecular weights have not been realized using free radical methods.

Anionic polymerization using addition type initiators, e.g., butyl lithium, $(\alpha MeS)_4$, living polystyrene, gave high conversion to high molecular weight polymers. On the other hand, electron transfer initiation resulted in very low yields of oligomeric products. The low solubility of **2** in solvents such as THF at low temperatures results in very low reaction rates. Low-temperature polymerization, <50 °C, was necessary because of the instability of the polymeric anion at higher temperatures. The polymerization at low temperatures proceeds in a heterogeneous system with the polymer anions in solution and the monomer supply coming from the insoluble monomer particles. The disappearance of the insoluble monomer is an indication of the conversion. In a typical anionic polymerization using $(\alpha MeS)_4{}^{2-}$, $2Na^+$ as initiator, THF as solvent at −60 °C, high conversion (>80%), high molecular weight ($\bar{M}_n$, $\bar{M}_w \sim 10^5$–10^6) polymers were obtained in 3–4 days. The poly-2-vinylanthracene was readily soluble and spectroscopic analysis was fully consistent with a conventional 1,2-vinyl structure. Molecular weight distributions were generally 2 or greater, reflecting the unusual nature of this anionic polymerization reaction.

Cationic polymerization of **2** proceeded readily in CH_2Cl_2 at a temperatures above 25° using $BF_3{\cdot}OEt_2$ as initiator. Conversions of 60–80% in 2–3 days were obtained and polymer molecular weights were generally low and in the range of $\bar{M}_n \sim 10^4$. The extremely low solubility of the monomer in typical solvents for cationic polymerization precluded polymerization at lower temperatures and was the major obstacle to achieving higher molecular weights. The polymers were again readily soluble.

All attempts to polymerize **2** with Ziegler–Natta catalysts, e.g., $AlEt_3/TiCl_4$ in benzene as solvent, resulted in high yields of insoluble products.

The anionic and cationic polymerization of 2-propenyl-2-anthracene (**3**) closely paralleled that of 2-vinylanthracene. Low monomer solubility necessitated long reaction times, particularly at lower temperatures. The carbanion of **3** was more stable than that from **2** and polymerization reactions could be run at −30 °C to give high molecular weight polymers, $\bar{M}_n \sim 10^5$ and $\bar{M}_w/\bar{M}_n \sim 2$. Free radical polymerization of **3** at temperatures above room temperature failed to yield any polymer.

Polymerization of 1-Vinylanthracene. The anionic polymerization of 1 was effected using $(\alpha MeS)_4{}^{2-}$, $2Na^+$, or living polystyrene in THF at −78 °C. Since the solubility of **1** is greater than that of **2**, the polymerization proceeds more readily and complete conversion is achieved in 1–2 days. The polymer is again completely soluble in common solvents. Molecular weights greater than $\bar{M}_n \sim 10^5$ were obtained with molecular weight distributions of 2 or greater, reflecting the long polymerization times. As with the 2-substituted vinylanthrancenes, polymerizations conducted at elevated temperatures were poorly reproducible and the products generally complex.

The achievement of high molecular weight polymers of 1- and 2-vinylanthracenes with conventional structures clearly demonstrates that in these systems under the appropriate conditions, the anomalous transfer and termination reactions involving the anthracene group are not significant. The generally broad molecular weight distributions reflect the very low monomer solubility and the unusual nature of these polymerizations. Termination and transfer processes become more significant at elevated temperatures. The most critical aspect of these polymerization reactions is the purity of the monomer. Reproducible results and high molecular weight, soluble polymers were obtained only with highly purified monomer samples. Deliberate exposure of monomer to air/light for short periods (5–15 min) resulted in anomalous polymerizations (including total inhibition) and polymeric products. One feature of these vinylanthracene polymers which should be emphasized is their facile photooxidation and photo cross-linking. The photodimerization of anthracenes[11] is well known. In the polymers this reaction leads to rapid insolubilization and polymer handling and characterization requires considerable caution.

The procedures developed here for the polymerization of the 1- and 2-vinylanthracenes were applied to a number of 9-vinylanthracene monomers.[12] Even with highly purified monomer, however, these polymerization reactions were more complex and the maximum molecular weights attained were in the range $\bar{M}_n \sim 1\text{–}5 \times 10^4$. The polymers were readily soluble and spectroscopic analysis was consistent with a conventional 1,2-vinyl structure.

The details of the polymerization reactions, the reaction mechanisms, and the polymer characterization will be the subject of a forthcoming series of publications.

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CORRECTIONS

"Charge-Induced Conformational Changes in Carboxymethylamylose", by P. L. Dubin and D. A. Brant, Volume 8, Number 6, November–December 1975, page 831.

One line of type has been omitted from the middle of the second column on page 840. The sentence beginning in line 27 should read:

Finally, we observe that the apparent discrepancy *between our results and those of Banks and Greenwood may arise from differences* in the integrity of the helical structure formed in the presence of BuOH by amylose and CMA.

"The ^{13}C NMR Spectrum of *N*-Ethyl-*N*-methylformamide", by J. G. Hamilton, K. J. Ivin, L. C. Kuan-Essig, and P. Watt, Volume 9, Number 1, January–February 1976, page 67.

We reported that in the ^{13}C{^{1}H} NMR spectrum of *N*-ethyl-*N*-methylformamide the intensity pattern of the four N–*C* lines was not of the back-to-back type. A further experiment using gated decoupling, with a delay time of 75 s between pulses, has shown that these four lines do in fact have a back-to-back intensity relationship, the earlier apparent anomaly for the NCH$_3$ lines being due to differential nuclear overhauser effects and relaxation times in the two conformers, which cause a reversal of relative intensities when the time between pulses is short. The proportions of the two conformers obtained from the gated-decoupling experiment were 62 and 38% (in $CDCl_3$ at 35 °C).