TABLE IX
A SUMMARY OF THE COPOLYMERIZATION PARAMETERS FOR PFS

M_1	M_2	r_1	r_2	Q_2	e_2	r_1r_2	ϕ
Styrene	PFS	0.43	0.22	0.69	0.74	0.095	7.2
Methyl methacrylate	PFS	0.98	0.90	0.87	0.75	0.89	5.3

fluorostyrene, and 0.22 for pentachlorostyrene.[19] Alfrey and Ebelke[20] have suggested that the reduced Q value of pentachlorostyrene results from a steric inhibition of resonance due to the *o*-chloro substituents. A similar explanation could be evoked for PFS.[26]

It is usually expected that a large tendency toward alternation of monomers in a copolymer will be reflected in a large value of ϕ. The data of Table IX do not accord with this expectation; the styrene copolymer, which is appreciably alternating, has a rather small ϕ value. Table X summarizes similar data for the literature. Walling[27] found that the ϕ for the styrene–diethyl fumarate system was surprisingly low despite the pronounced alternating tendency of the copolymer. Apparently, the radical recombination reaction is far less sensitive to polar factors than is the more activated addition to a double bond.

TABLE X
VALUES OF THE CROSS-TERMINATION CONSTANT ϕ

System	ϕ	r_1/r_2
PFS–styrene[a]	7.2	0.095
PFS–MMA[a]	5.3	0.89
p-Methoxystyrene–styrene[b]	1.0	0.95
p-Methoxystyrene–MMA[b]	24	0.09
Styrene–MMA[b]	14	0.26
Styrene–diethyl fumarate[c]	8	0.028
Styrene–butyl acrylate[b]	150	0.07

[a] Present value. [b] G. M. Burnett, "Mechanism of Polymer Reactions," Interscience Publishers, New York, N.Y., 1954, pp 295–297. [c] See ref 27.

(26) Atomic radii (angstroms) are H, 0.28; F, 0.64; Cl, 0.99: "Tables of Interatomic Distance and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London.

(27) C. Walling and E. A. McElhill, *J. Amer. Chem. Soc.*, 73, 2819 (1951).

Simultaneous Cationic Homopolymerizations of Vinylcarbazole and Oxetane

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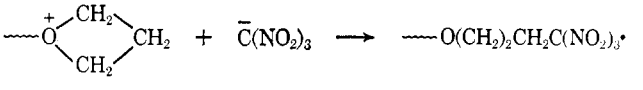
ABSTRACT: Polymerization of vinylcarbazole and oxetane was initiated in nitrobenzene by tetranitromethane (TNM). It was shown that nitroform is the probable initiator, the latter being formed by the sequence

$$C(NO_2)_4 + CH_2{=}CHN{<} \rightarrow C(NO_2)_3^- + NO_2CH_2CH^+N{<} \rightarrow HC(NO_2)_3 + NO_2CH{=}CHN{<}$$

The uptake of both monomers was followed by nmr technique; thus $-d[V]/dt$ and $-d[Ox]/dt$ were determined simultaneously. The reaction produces a mixture of two homopolymers. Although the presence of oxetane reduced the rate of vinylcarbazole polymerization by a factor of 30, it did not affect its molecular weight. The polymerization of vinylcarbazole is first order in TNM and in monomer; the termination apparently involves a "wrong" monomer addition. The polymerization of oxetane requires the presence of vinylcarbazole; TNM alone does not initiate the reaction. Its rate is proportional to $[TNM]^{1/2}$, $[V]^{1/2}$ and [Ox], indicating bimolecular termination arising from combination of the ions. The kinetic results demonstrate that oxetane is about 30 times more reactive toward nitroform than vinylcarbazole.



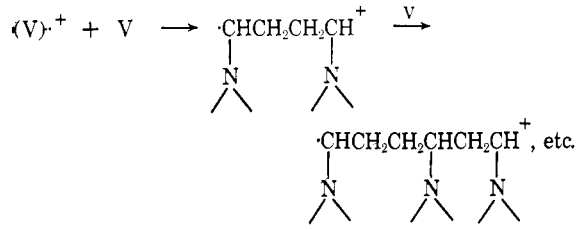
Polymerization of vinylcarbazole initiated in nitrobenzene by tetranitromethane was studied by Pac and Plesch,[1] who found the reaction to be first order in the initiator and monomer. The molecular weight of the resulting polymer was independent of the concentration of the initiator but increased with concentration of the monomer. The following mechanism was proposed. Tetranitromethane (TNM) and vinylcarbazole (V) form reversibly charge-transfer complex which slowly decomposes into positive $(V)\cdot^+$ and negative $(TNM)\cdot^-$ radical ions. The former initiate cationic polymerization, namely

(1) J. Pac and P. H. Plesch, *Polymer*, 8, 252 (1967).

TABLE I
POLYMERIZATION OF VINYLCARBAZOLE AND OXETANE IN NITROBENZENE AT 10° [a]
(TETRANITROMETHANE CATALYST)

$[TNM]_0 = 4.5 \times 10^{-4} M$			$[TNM]_0 = 5 \times 10^{-3} M$			$[TNM]_0 = 10 \times 10^{-3} M$		
Time, min	[V], *M*	[Ox], *M*	Time, min	[V], *M*	[Ox], *M*	Time, min	[V], *M*	[Ox], *M*
0	0.635	0.715	0	0.63	0.76	0	0.51	0.63
4	0.62	0.66	1	0.61	0.75	0.5	0.48	0.61
11	0.605	0.66	2	0.59	0.73	1.0	0.46	0.61
19	0.56	0.62	3	0.53	0.71	1.5	0.44	0.59
20	0.575 (?)	0.61	4	0.50	0.70	2.0	0.385	0.585
38	0.49	0.57	5	0.49	0.65	4.5	0.275	0.56
42	0.49	0.56	6	0.45	0.65	5.5	0.26	0.54
47		0.55	9	0.39	0.60	6.0	0.26	0.53
52	0.475	0.53	12	0.35	0.57	6.5	0.25	0.52
59	0.46	0.52	15	0.32	0.52	8.5	0.18	0.495
67	0.47	0.50	20	0.25	0.47	12.5	0.16	0.44
72	0.45	0.49	23	0.21	0.45	18.5		0.40
83	0.43	0.48	26	0.19	0.44	22.5	0.14	0.36
92	0.42	0.47	29	0.18	0.42			
96	0.43	0.46						
102	0.40	0.46						
107	0.40	0.44						

[a] $[V]_0/[Ox]_0 \approx 1$; $[TNM]_0$ variable.



The radical ends of the polymer are rapidly inactivated by the excess of TNM which supposedly acts as a radical trap. The fate of radical anions was not specified. The propagation was assumed to be terminated by "wrong" monomer addition.

The suggested mechanism implies that a simultaneous anionic and cationic polymerization could be induced in the above system provided a suitable monomer is added to the reagents. We attempted to initiate anionic polymerization of nitroethylene under these conditions, and since the results were negative it was decided to reexamine the mechanism of tetranitromethane initiation.

It seems that TNM does not form radical anions—the electron capture is dissociative,[2] $C(NO_2)_3^-$ and NO_2 being the products. TNM may react, nevertheless, with suitable electron donors and form a charge-transfer complex; *e.g.*, its addition to 1,1-diphenylethylene in nitrobenzene instantaneously produces a complex absorbing at $\lambda_{max} = 410$ mμ. Studies of Penczek, *et al.*,[3] demonstrated that the complex slowly decomposes

$$\{(TNM)(CH_2{=}CPh_2)\} \rightarrow {}^+C(Ph)_2CH_2NO_2 + C(NO_2)_3^- \quad (1)$$

and the intermediate carbonium ion deprotonates giving the final products of the reaction, *i.e.*

$${}^+C(Ph)_2CH_2NO_2 + C(NO_2)_3^- \rightarrow C(Ph)_2{=}CHNO_2 + HC(NO_2)_3 \quad (2)$$

It is probable that the polymerization of vinylcarbazole is initiated by a similar NO_2^+ transfer, and not by a direct electron transfer. The resulting car-

$$\{(V)(TNM)\} \rightarrow {>}N^+CHCH_2NO_2 + C(NO_2)_3^- \rightarrow {>}NCH{=}CHNO_2 + HC(NO_2)_3$$

bonium ion or the nitroform may lead then to propagation, the former directly adding the monomer and the latter initiating propagation through proton transfer to vinylcarbazole. The formation of nitroform was confirmed in the course of this work. The nmr spectrum of nitroform in nitrobenzene at 10° gives a single sharp line at 530 cps. The same line, although much broader, was observed in the spectrum of the products of the reaction of 1,1-diphenylethylene with TNM in nitrobenzene.

Experimental Section

Commercial vinylcarbazole was twice recrystallized from *n*-pentane. Oxetane was fractionated, refluxed with sodium benzophenone and redistilled. Its purity was ascertained by vpc using a castor wax column. Tetranitromethane was washed with dilute KOH, water, thereafter dried with molecular sieves, and finally sublimed on a high-vacuum line into storage capillaries.

The polymerization was investigated in nitrobenzene. The solvent was crystallized by its partial freezing, twice distilled from BaO on a high vacuum line and finally sealed in ampoules equipped with break-seals.

The required solutions were prepared on a high-vacuum line, mixed in a special device and then immediately frozen with liquid air in nmr tubes which were sealed off. The progress of polymerization was followed by nmr technique.

(2) G. H. J. Bielski and A. G. Allen, *J. Phys. Chem.*, 71, 4545 (1967).

(3) S. Penczek, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, 90, 2174 (1968).

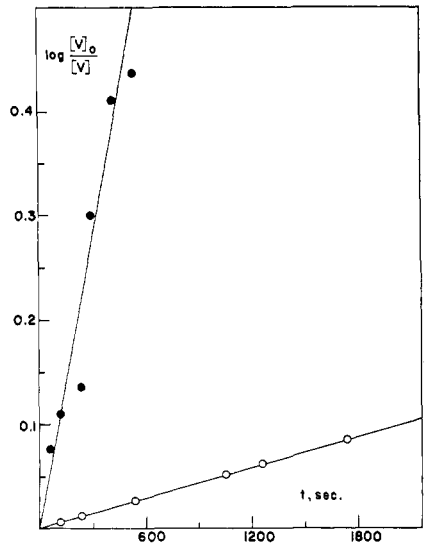


Figure 1. Plots of log $[V]_0/[V_t]$ *vs.* time for $[Ox]_0 = 0$ and 0.45 *M*; $[TNM]_0 = 5.0 \times 10^{-4}$; $[V]_0 = 1$ *M*.

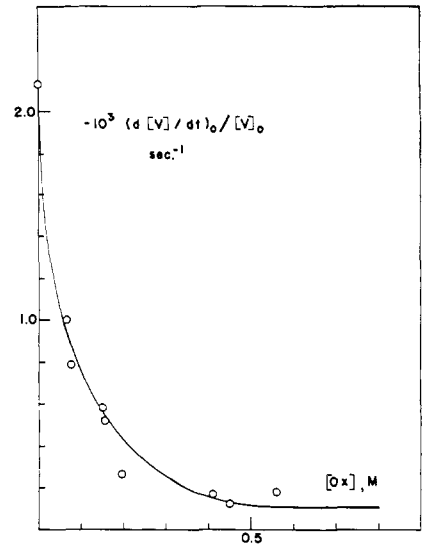


Figure 2. Plot of $[dV/dt]_0/[V]_0$ *vs.* $[Ox]_0$. $[TNM]_0 = 5.0 \times 10^{-4}$ *M* and $[V]_0 = 1$ *M*.

The nmr tubes were warmed up, in turn, and thereafter they were immediately inserted into the cavity of an A-60-A Varian spectrometer. The cavity was thermostated at 10°. The first spectrum was recorded in about 2 min after removing the tube from a dewar. Thereafter, the spectra were periodically recorded at desired intervals (see, *e.g.*, Table I).

The concentration of the unpolymerized vinylcarbazole was determined by integrating the four bands due to olefinic protons. Integration of the α protons of oxetane allowed us to determine the concentration of the unreacted oxetane. On polymerization both signals are substantially shifted upfield. The nmr measurements were standardized with the aid of solutions of the reagents and products of known concentrations. Polymerization increases the macroscopic, but not the microscopic, viscosity of the solution; hence, the width of the nmr lines of the monomer is not affected by the reaction. The applied method is unique because it allows one simultaneous determination of the concentration of both monomers in the course of polymerization.

Results

The first-order kinetics of vinylcarbazole polymerization were confirmed. This is shown by Figure 1. The formal rate constant, defined by $-d[V]/dt = k_V[TNM][V]$, was found to be 4.3 M^{-1} sec^{-1} at 10°, whereas a value of 11 M^{-1} sec^{-1} at 34° was reported by Pac and Plesch.[1]

The addition of oxetane retards the polymerization of vinylcarbazole, this being seen by inspection of Figure 1. The retardation does not affect the first-order kinetics of vinylcarbazole consumption provided the concentration of oxetane is sufficiently high. The simultaneous polymerization of both monomers produces a mixture of two homopolymers. For example, a product composed of about 50:50 mixture of both units was separated into soluble and insoluble fractions by extraction with methanol and acetone. The insoluble fraction contained virtually all of the polyvinyl carbazole and less than 10% of polyoxetane (probably a nonextracted homopolymer).

The molecular weights of three batches of the polyvinylcarbazole resulting from polymerization performed at the same initial concentration of the monomer and TNM were determined by the viscometric method (see Table II). The first two samples were obtained in the absence of oxetane, while the last was produced in the presence of an equimolar amount of the ether. Although the addition of oxetane reduced the rate of polymerization of vinylcarbazole by a factor of 30, its molecular weight was not affected (see Table II). Apparently oxetane does not compete with vinylcarbazole for the growing polyvinylcarbazole; the retardation of vinylcarbazole polymerization must be attributed, therefore, to a competition of both monomers for the initiating species.

The dependence of the initial "first order" constant, $(-d[V]/dt)_0/[V]_0$, of vinylcarbazole polymerization on the initial concentration of oxetane is shown in Figure 2. The initial concentrations of vinylcarbazole and TNM were kept constant, namely, 1 and 5×10^{-4} *M*, respectively, while the concentration of oxetane was varied. The results were replotted in Figure 3 giving $[V]_0[TNM]_0/(-d[V]/dt)_0$ as a function of $[Ox]_0/[V]_0$. In spite of some scatter observed at high ratios of $[Ox]_0/[V]_0$ (this is not surprising in view of the mathematical form of the calculation—compare Figures 2 and 3), the linearity of this relation is established. Its significance will be elaborated in the discussion.

TABLE II

MOLECULAR WEIGHT[a] OF POLYVINYLCARBAZOLE DETERMINED FROM ITS INTRINSIC VISCOSITY ACCORDING TO THE EQUATION[b] $[TNM] = 5 \times 10^{-4}$ *M* (CONVERSION 60%)

Run	$[V]_0$, *M*	$[Ox]_0$, *M*	$\bar{M}_V$ (poly-V)
1	0.70	0.0	180,000
2	0.68	0.0	150,000
3	0.68	0.75	160,000

[a] The molecular weight of the isolated polyoxetane was 3500. The reported results were reproduced twice. [b] K. Ueberreiter and J. Springer, *Z. Phys. Chem.*, **36**, 299 (1963).

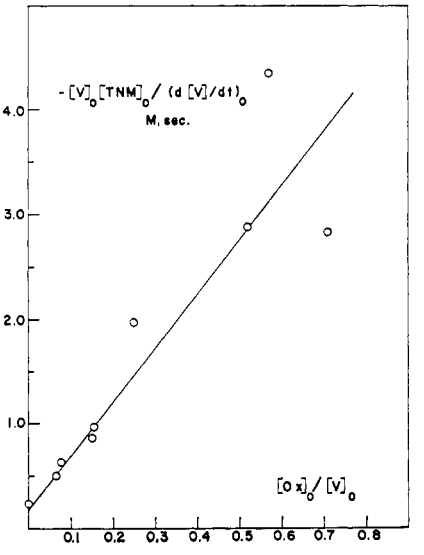


Figure 3. Plots of $[V]_0[TNM]_0/[dV/dt]_0$ *vs.* $[Ox]_0/[V]_0$; slope/intercept = 28.6.

The dependence of the rate of polymerization of oxetane on the concentration of vinylcarbazole was investigated in another series of experiments. Tetranitromethane *does not* initiate polymerization of oxetane, although the reaction ensues if 1,1-diphenylethylene[3] or vinylcarbazole is added to nitrobenzene–oxetane–tetranitromethane mixtures. This indicates that the carbonium ions produced in the initiation step of vinylcarbazole polymerization, or nitroform formed by their deprotonation, are the direct initiators of oxetane polymerization.

Figure 4 shows that log $(-d[Ox]/dt)_0$ is linear with log $[V]_0$, the slope being one-half. Hence, $(-d[Ox]/dt)_0$ = constant $[V]_0^{1/2}$. The apparent rate constants of the respective polymerizations are defined as $k_{ap} = -(d[V]/dt)/[V]$ for vinylcarbazole and $k_{ap} = -(d[Ox]/dt)/[Ox][V]^{1/2}$ for oxetane. Their dependence on [TNM] for approximately constant $[V]_0$ and $[Ox]_0$ is shown in Figure 5, the data being taken again from Table I. For vinylcarbazole, k_{ap} is proportional to the first power of [TNM], whereas for oxetane k_{ap} is proportional to the square root of TNM concentration.

Mechanism of "Copolymerization" of Vinylcarbazole and Oxetane. The results of this study demonstrate that two simultaneous homopolymerizations are initiated by tetranitromethane in a mixture of vinylcarbazole and oxetane. The behavior of the system TNM + 1,1-diphenylethylene suggests that the reactions

$$C(NO_2)_4 + V \underset{}{\overset{K_1}{\rightleftharpoons}} \text{charge-transfer complex} \xrightarrow{k_2} NO_2CH_2CH^+N< + C^-(NO_2)_3$$

and

$$NO_2CH_2CH^+N< + C^-(NO_2)_3 \xrightarrow{\text{rapid}} NO_2CH{=}CHN< + CH(NO_2)_3$$

produce the ultimate initiator, namely, nitroform. Indeed, independent experiments, to be reported later, proved that nitroform efficiently initiates the polymerization of either of these two monomers, presumably through a proton transfer, *i.e.*

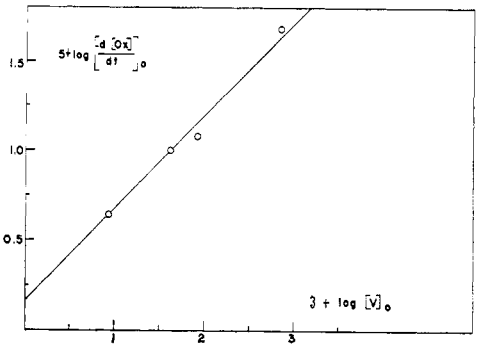


Figure 4. Plot of $[-(d[Ox]/dt)]_0$ *vs.* $[V]_0$; $[TNM]_0 = 8 \times 10^{-3}$ *M*; $[Ox]_0 = 0.7$ *M*.

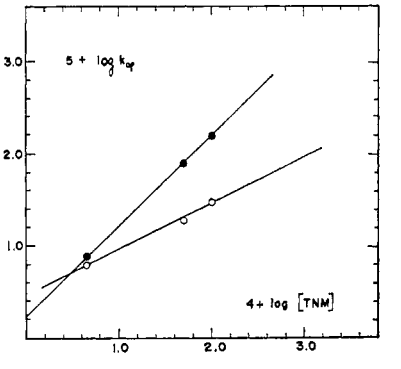
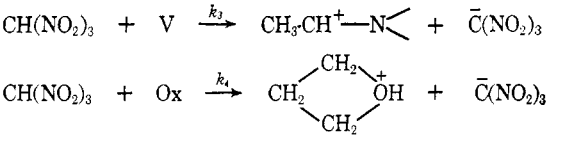
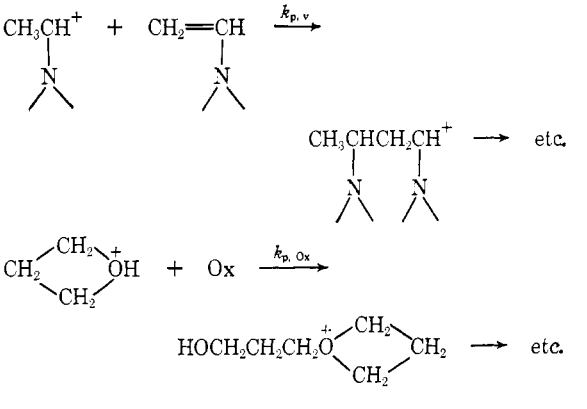


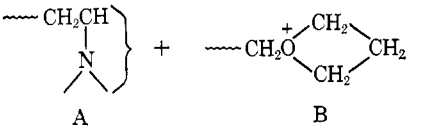
Figure 5. Plots of log k_{ap} *vs.* log [TNM] for oxetane (○) and N-vinylcarbazole (●).



The resulting cations propagate the reaction, *i.e.*



It is assumed that both propagations involve free ions because the nitroform salts of the *conjugated* carbonium ions (A) and of the bulky oxonium ions (B) probably are completely dissociated in nitrobenzene (at least at the

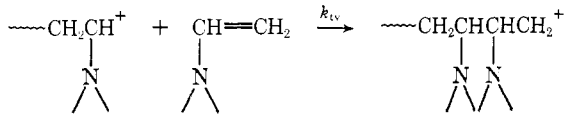


A B

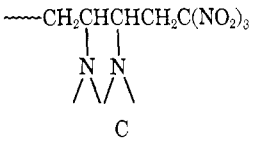
concentrations prevailing in the polymerization).

Kinetic data show the propagation of vinylcarbazole polymerization to be terminated by a "wrong" mono-

mer addition. The head-to-head addition probably accounts for this event, *i.e.*

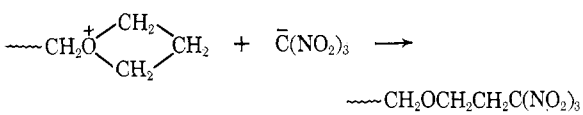


the resulting carbonium ion being rapidly associated with $C^-(NO_2)_3$ and thus an inactive, covalently bonded product (C) is formed. The oxonium ions also may



C

be inactivated by $C^-(NO_2)_3$; however, in this system the process



is rate determining for the termination.

The molecular weight of polyvinylcarbazole formed in the mixture of monomers is independent of oxetane concentration although the presence of the ether may reduce the rate of vinylcarbazole consumption by a factor as large as 30. This is a remarkable finding. It indicates that oxetane does not react with the growing polyvinylcarbazole cations; nevertheless, it competes efficiently with vinylcarbazole for the nitroform. This result implies that $NO_2CH_2CH^+N<$ carbonium ion probably is not the initiator of oxetane polymerization and this led us to postulate the initiation by nitroform.

It is probable that vinylcarbazole does not interfere with the growth of polyoxetane cation. Unfortunately, direct evidence is not available because tetranitromethane does not initiate the polymerization of this ether in the absence of vinylcarbazole. Furthermore, a rapid chain transfer to monomer, which occurs in oxetane polymerization, makes the determination of the molecular weight of polyoxetane of little value.

The proposed mechanism, in conjunction with the hypothesis of stationary state, leads to the kinetic expression

$$-d[V]/dt = (K_1k_2k_{p,v}/k_{t,v})[TNM][V] / \{1 + k_4[Ox]/k_3[V]\}$$

i.e., the plot $-[TNM]_0[V]_0/(d[(V]/dt)_0$ *vs.* $[Ox]_0/[V]_0$ should give a straight line with intercept $k_{t,v}/K_1k_2k_{p,v}$ and slope (k_4/k_3) (intercept). This is shown in Figure 3 from which the value of about 30 is obtained for k_4/k_3 and about 5 M^{-1} sec^{-1} for $k_v = K_1k_2k_{p,v}/k_{t,v}$.

The bimolecular termination of oxetane polymerization leads to the equation

$$-d[Ox]/dt \approx \{K_1k_2k^2_{p,Ox}/k_{t,Ox}\}^{1/2} \times [TNM]^{1/2}[V]^{1/2}[Ox]\{(1 + k_3[V])/k_4[Ox]\}^{1/2}$$

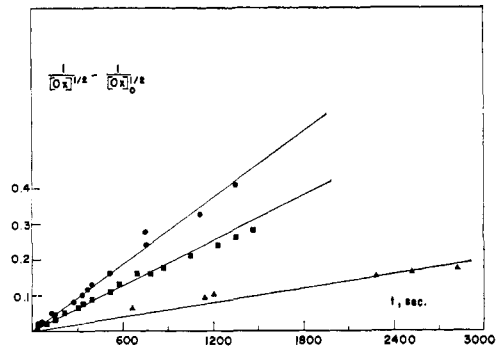


Figure 6. $(1/[Ox][^{1/2} - (1/[Ox]_0^{1/2}$ *vs.* time; $[V]_0 = 0.818$ *M*; $[Ox]_0 = 0.901$ *M*; ●, ■, and ▲ refer to $[TNM]_0 = 1.0 \times 10^{-2}$, 5×10^{-3}, and 5×10^{-4} *M*, respectively.

if one accepts the reasonable approximation [growing polyoxetane] = $[C^-(NO_2)_3]$. Under our experimental conditions $k_3[V]/k_4[Ox] \ll 1$, and thus the observed dependence of $-d[OX]/dt$ on the square root of vinylcarbazole concentration (see Figure 4) and on $[TNM]^{1/2}$ (see Figure 5) is rationalized. In experiments listed in Table I the ratio $f = [V]/[Ox]$ is approximately constant, at least at the early stages of the reaction. Since

$$-d[Ox]/dt \approx \text{constant } [TNM]^{1/2}[Ox]^{3/2}f^{1/2}$$

one finds

$$(1/[Ox]^{1/2}) - (1/[Ox]_0^{1/2}) = \text{constant } [TNM]^{1/2}\left(\int_0 f^{1/2}dt\right)/t$$

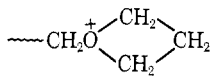
where the constant is $(K_1k_2k_{p,Ox}^2/k_{t,Ox})^{1/2}$. The term

$$\left(\int_0^t f^{1/2}dt\right)/t$$

does not vary too much in each individual run and therefore the plot of $(1/[Ox]^{1/2}) - (1/[Ox]_0^{1/2})$ *vs.* time is approximately linear. This is shown in Figure 6, and the slopes of the respective lines were used to calculate k_{ap} values plotted in Figure 5.

Finally, simultaneous homopolymerization of two monomers propagated by the *same* (cationic) mechanism calls for comments. Two homopolymerizations propagated in the same solution by two different mechanisms are possible, *e.g.*, they were observed by Gilbert, *et al.*[4]

The problem is more complex in our system. Polymerization of oxetane involves an oxonium ion (D) which reacts with the basic oxetane but not with the

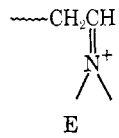


D

vinyl monomer. Therefore, why does not the more basic oxetane compete with vinylcarbazole for the growing polyvinylcarbazole cation?

(4) H. Gilbert, F. F. Miller, S. J. Averill, E. J. Carlson, V. L. Folt, H. J. Heller, F. D. Stewart, R. F. Schmidt, and H. L. Trumbull, *J. Amer. Chem. Soc.*, 78, 1669 (1956).

The following tentative suggestion is offered. The polyvinylcarbazole cation is very inert; it may be represented as an ammonium ion E. Consequently,



E

it is incapable of initiating propagation in the absence of some additional driving force. Such a force may be provided by the polarizability of the planar vinylcarbazole molecule by the planar carbonium ion of polyvinylcarbazole. This additional driving force does not operate in the addition of oxetane. Hence, homopropagation of vinylcarbazole, but not its copolymerization with oxetane, is feasible.

The importance of polarizability in some reactions of planar aromatic molecules was demonstrated elsewhere.[5]

Acknowledgment. We gratefully acknowledge the financial support of this investigation by the National Science Foundation and the Petroleum Research Fund administered by the American Chemical Society.

(5) J. Stearne, J. Smid, and M. Szwarc, *Trans. Faraday Soc.*, 62, 672 (1966)

Polymerization and Copolymerization of N-Vinylindole and N-Vinylmethylindoles

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ABSTRACT: Polymers and copolymers of N-vinylindole, N-vinyl-2-methylindole and N-vinyl-3-methylindole have been synthesized. The synthetic procedures for preparing the monomers and the polymers are described.

As part of an investigation of the polymerizability of N-vinyl heterocyclic compounds, the homopolymerization and copolymerization of N-vinylindole, N-vinyl-2-methylindole, and N-vinyl-3-methylindole were studied. The polymerization of N-vinylindole with stannic chloride[1] and with organic electron acceptors[2] to give polymers in the molecular weight range 600–1800 and 5400, respectively, has recently been reported. The polymer was described as a white powder softening between 169 and 177°.[1]

The monomers N-vinylindole, N-vinyl-2-methylindole, and N-vinyl-3-methylindole were prepared by the vinylation of indole,[3] 2-methylindole,[4] and 3-methylindole, respectively, at 150–190° and 20–30 atm pressure. The three monomers were successfully polymerized thermally without added catalyst and with cationic, free-radical, radical-cation and Ziegler–Natta catalysts. The number average molecular weight of several of these polymers were greater than 10,000 as determined by vapor phase osmometry and confirmed by gel permeation chromatography.

The polymerization data which are summarized in Table I indicated that N-vinylindole is polymerized more readily than the 2- or 3-methyl derivatives. Apparently α and β substituents on the indole ring affect the monomer reactivity in a manner similar to that of *ortho* and *meta* substituents on styrene.[5] This is further substantiated by the unsuccessful attempts to copolymerize N-vinyl-2-methylindole with N-vinyl-3-methylindole and by the poor yields obtained in attempting to copolymerize N-vinylindole with either monomer.

Of considerable interest was the copolymerization of N-vinylindole with monomers having a reactive double bond within the ring structure. It was found that copolymers could be prepared with indole, N-methylindole, indene, coumarin and maleic anhydride (Table II). Elemental analyses (Table III) suggest that approximate 1:1 copolymers were prepared using 1:1 molar quantities of monomers. Copolymer formation was confirmed by the following experimental evidence: the C, H, and N analyses and the infrared spectra of the copolymers were unchanged after Soxhlet extraction with boiling methanol for 144 hr. Attempts to homopolymerize the comonomers indole, N-methylindole, coumarin, and indene under the same conditions used for the copolymerization and for the homopolymerization of N-vinylindole were unsuccessful. Each monomer was recovered quantitatively, unchanged. The single gel permeation chromatographic distribution peaks obtained for each copolymer were examined by computer programmed analysis.[6] These results gave

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