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Acrylonitrile Copolymerizations. V. Anomalous Kinetics and Secondary Reactions in Copolymerization with Vinyl Chloride

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ABSTRACT

Kinetic deviations from the Lewis and Mayo theory for the radical copolymerization of acrylonitrile and vinyl chloride reported previously are tentatively interpreted as a consequence of an internal transfer reaction involving the tertiary hydrogen atom of an antepenultimate acrylonitrile unit. Although the deviations disappear if acrylonitrile is replaced by methacrylonitrile, this interpretation is far from being quantitatively satisfactory. Another explanation seems to be better: it involves intramolecular copolymerization with C≡N triple bonds producing a cyclic imine radical which gives rise to coloration of the copolymer and causes the formation of new $-C{=}N^{\cdot}$ radicals with low reactivity vs propagation reactions.

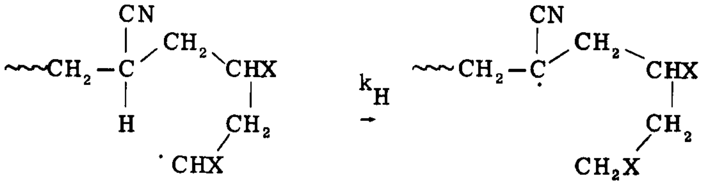
INTRODUCTION

In a previous paper [1] it was shown that very large deviations from the simple Lewis and Mayo theory occur in the kinetics of radical copolymerization of vinyl chloride (C) and acrylonitrile (A) in dimethylformamide (DMF) solution. These anormalous kinetics have been interpreted in terms of the penultimate effect theory [2], and by using the Barb equation the following results were obtained for the four reactivity ratios: $r_{AA} = 4.0$, $r_{CA} = 2.5$, $r_{AC} = 3.0$, and $r_{CC} = 0.03$.

These results do not agree with the data reported by Thomson and Raines [3] for bulk polymerization, but they obey the Lewis and Mayo theory for the values of $r_A = 3.6$ and $r_C = 0.05$ for the two reactivity ratios.

The largest deviations between bulk and solution experiments occur in the intermediate composition range where the consumption of acrylonitrile is higher in solution by a factor of up to 1.6. We have checked some of the data of Thomson and Raines in bulk, and it appears as a rather large solvent effect. This suggests that secondary reactions might be involved which may be caused either by the solvent itself or by the dilution. The solvent may be a transfer agent, but actually the transfer constant [4] for the acrylonitrile or the vinyl chloride radical to DMF is not large enough to explain any anomalous behavior in the relative propagation rate. DMF has been shown [5] from viscosity measurements to form a complex with A, but the complex is stable only at low temperature. The viscosities of mixtures of A and DMF do not show any anomaly above room temperature. We were therefore inclined to consider the secondary reaction which may be enhanced by a dilution effect.

There might be an internal transfer reaction involving the α proton of an antepenultimate acrylonitrile unit. The scheme is

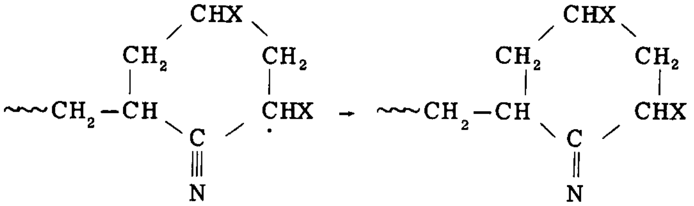


(1)

where X is either CN or Cl. Such a reaction gives rise to the formation of small branches. It has been shown previously that it gives a good quantitative explanation of similar (but less important) kinetic deviations in the radical copolymerization of vinyl chloride and vinyl acetate [6]. In order to test this reaction, three kinds of experiments have been carried out:

1. Radical copolymerization of vinyl chloride and methacrylonitrile.
2. New kinetic studies at various dilutions.
3. Transfer studies of vinyl chloride radical polymerization on isobutyronitrile.

Another secondary reaction has been suggested for acrylonitrile homopolymerization: copolymerization involving the C≡N triple bond. Such a reaction, first suggest by Brandrup et al. [7] as an intermolecular reaction, has been shown more recently by Patron et al. [8] to be an intramolecular reaction. The scheme is



(2)

This reaction gives rise to a new radical with a reactivity very different from the regular polyacrylonitrile or polyvinyl chloride radicals. It may undergo isomerization in its enaminonitrile structure or further reactions involving vicinal CN groups, all together leading to absorption in the UV and visible range of the spectra. It is also very reactive in cross-termination reactions, and causes a decrease of the overall reaction rate and a decrease of molecular weight. Therefore, in order to test the reaction, another set of experiments has been carried out:

1. Examination of the IR and UV spectra of the copolymers.
2. Study of the reaction rates.
3. Study of the molecular weights.

These experiments lead to the conclusion that the high reactivity of the vinyl chloride radicals enhanced the probability of the intramolecular copolymerization reaction.

RADICAL COPOLYMERIZATION OF VINYL CHLORIDE AND METHACRYLONITRILE

The experiments have been carried out at 60°C in DMF solution and followed kinetically using the gas chromatographic analysis of the monomer mixture, as is usual in our laboratory [1, 6]. The charge of

TABLE 1. Charge and Chromatographic Kinetic Results in the Methacrylonitrile (M) Vinyl Chloride (C) Copolymerization

M (moles)	C (moles)	DMF (moles)	$x_M = M/C$	$n_M = dM/dC$	Conversion (%)	
					M	C
0.014	0.577	4.24[a]	0.0242	0.103	31.2	7.3
0.034	0.678	5.12	0.050	0.209	21.3	5.1
0.137	0.464	5.43[b]	0.295	1.23	5.0	1.2
0.149	0.446	5.31	0.334	1.04	22.6	7.25
0.508	0.236	5.20	2.152	8.94	16.1	4.2
0.566	0.082	5.11	6.9	28.13	19.3	11.1
0.692	0.033	5.02	20.96	80	18.1	7.9

[a] In acetamide diethyl solution.
[b] In acetone solution.

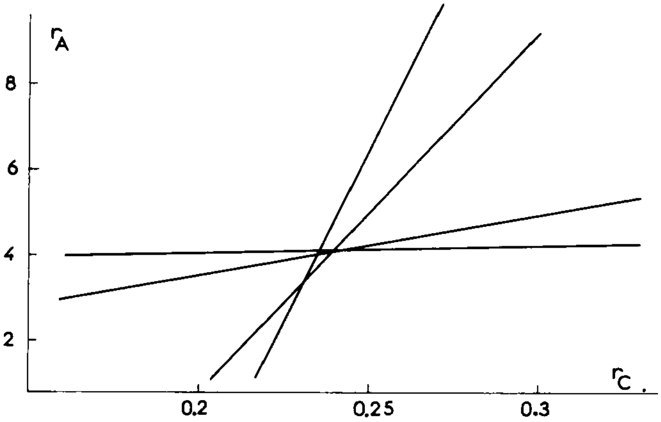


FIG. 1. Lewis and Mayo plot for methacrylonitrile-vinyl chloride copolymerization.

the reactor, together with the kinetic results for the instantaneous relative consumption of the monomers, are reported in Table 1. A Lewis and Mayo plot is given in Fig. 1 from which the following reactivity ratios are obtained:

r_M (methacrylonitrile) = 4.0 ± 0.1

r_C (vinyl chloride) = 0.237 ± 0.002

The Lewis and Mayo plot is well obeyed in the whole range of monomer feed composition. There are no anomalous kinetics in this system as would be expected if the reason for the deviation in the case of acrylonitrile copolymerization was either an internal transfer on the tertiary hydrogen atom or an internal copolymerization with the nitrile group. Indeed, this last reaction has not been shown to occur in the homopolymerization of methacrylonitrile [9].

INFLUENCE OF DILUTION ON KINETICS

The kinetic scheme assuming hydrogen transfer from an antepenultimate unit has been derived previously and applied to the copolymerization of vinyl chloride and vinyl acetate [6].

It involves a new radical B resulting from the formation of a short branch after the transfer step (1) which occurs with a rate constant k_T. The corresponding equation is

$$n_A = \frac{1 + r_A x}{\left(1 + \frac{r_C}{x}\right)\left[1 - \frac{\alpha\gamma}{\beta}\frac{k_T}{k_{cc}C}\right] + \frac{\gamma}{\beta}\frac{k_T}{k_{cc}C}} \tag{3}$$

where $n_A = dA/dC$; $x = A/C$; $\alpha = r_B x/(1 + r_B x)$;

$$\beta = 1 + \frac{x}{r_C} + \frac{kT}{k_{cc}C}$$

$$\gamma = r_A x + \frac{r_C}{r_C + x}$$

r_B is the reactivity ratio for the new radical $r_B = k_{BA}/k_{BC}$, k_{cc} is the vinyl chloride homopolymerization rate constant, and A and C are the concentrations of acrylonitrile and vinyl chloride monomers, respectively.

The extrapolation procedures of n_A/x vs x or $1/x$ for $x \to 0$ or $x \to \infty$, shown in Figs. 2 and 3, using the data previously published [1], gives $r_A = 3.9 \pm 0.1$ and $r_C = 0.03$.

A best fitting process allows an estimate of the two others parameters: $r_B = 0.4$ and $k_T/k_{cc} = 5$.

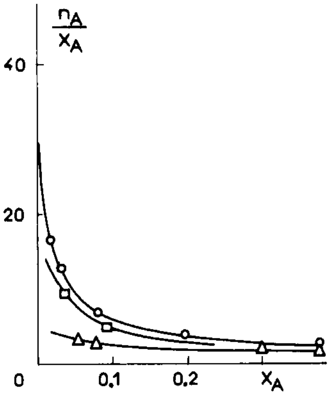


FIG. 2. Vinyl chloride-acrylonitrile copolymerization. Plot of n_A/x vs x for a total monomer concentrations of 2 moles/liter (○); 1.2 moles/liter (□)/ and 0.7 mole/liter (△).

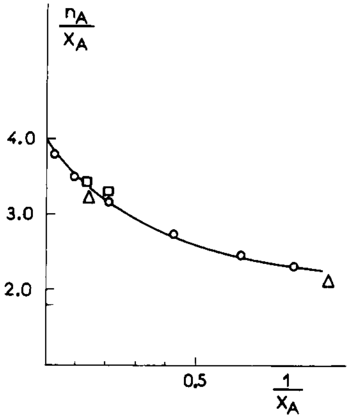


FIG. 3. Vinyl chloride-acrylonitrile copolymerization. Plot of n_A/x vs $1/x$ for a total monomer concentration of 2 moles/liter (○); 1.2 moles/liter (□); and 0.7 mole/liter (△).

The value of r_B would be expected to be close to the r_A and r_M values because the new branched radical is not very different in structure from the regular acrylonitrile or methacrylonitrile radicals. However, a factor of 10 is obtained in the best fitting process.

The value of k_T/k_{cc} (i.e., the transfer constant) is estimated to be very high; however, high polymers are obtained. Furthermore, Eq. (3) predicts, owing to the last term in the denominator, that the composition would be concentration dependent. A new set of experiments has been carried out in DMF solution at 60° C at various dilutions. The results are illustrated in Figs. 4 and 5 as a square composition diagram and as Fineman-Ross plots, respectively. Although there is an obvious concentration dependence, as predicted by Eq. (3), the results are far from satisfactory on the quantitative point of view, as shown in Table 2. No other set of values gives better agreement.

ISOBUTYRONITRILE AS A TRANSFER AGENT IN VINYL CHLORIDE POLYMERIZATION

Isobutyronitrile may be considered as a good model compound for a hydrogen transfer reaction involving the α proton of an acrylonitrile unit in a copolymer. It has been used for this reason in a number of acrylonitrile copolymerizations [10] but not for vinyl chloride. Vinyl chloride homopolymerization experiments have therefore been carried out at 60°C in dichloroethane as solvent in the presence of various

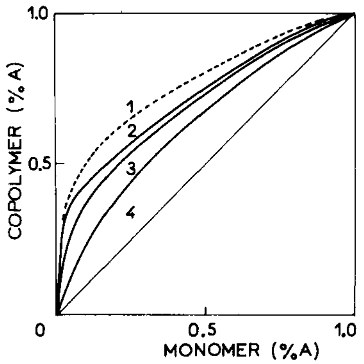


FIG. 4. Vinyl chloride-acrylonitrile copolymerization. Composition of the copolymer vs composition of the monomer feed (mole %) for various overall monomer concentrations. (1) Bulk copolymerization, (2) 2 moles/liter, (3) 1.2 moles/liter, and (4) 0.7 mole/liter.

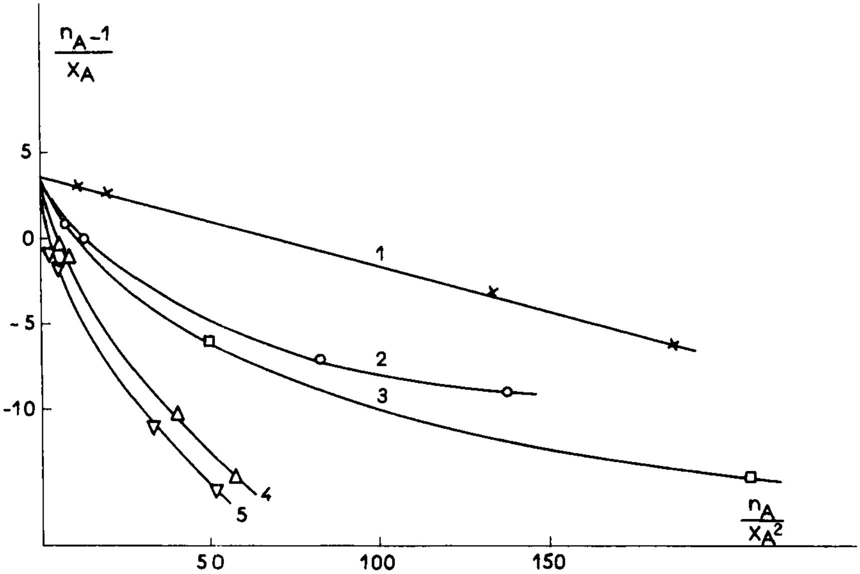


FIG. 5. Fineman-Ross plot of vinyl chloride-acrylonitrile copolymerization. Bulk copolymerization (1). Solution in dimethylformamide, overall monomer concentration: 2 moles/liter (2), 1.2 moles/liter (3), 0.7 mole/liter (4), and 0.3 mole/liter (5).

TABLE 2. Vinyl Chloride-Acrylonitrile Copolymerization in Dimethylformamide Solution. Interpretation of Dilution Experiments According to the Hydrogen Transfer Hypothesis ($r_A = 3.9$, $r_B = 0.4$, $r_C = 0.03$, $k_T/k_{cc} = 5$)

		n_{cal}	
x_A	n_{ex}	Classical	Transfer
	2 moles/liter		
33.3	127.5	131	79.5
10.5	36.8	41.8	26.35
4.8	15.1	19.6	12.88
2.36	6.5	10.0	6.99
1.54	3.77	6.8	4.94
0.94	2.36	4.5	3.38
0.79	1.82	3.93	2.98
0.536	1.6	2.93	2.28
0.195	0.78	1.33	1.27
0.08	0.545	0.95	0.81
0.03	0.376	0.56	0.47
0.019	0.316	0.41	0.36
0.26[a]	1.62	1.8	1.48
0.084[a]	0.77	0.98	0.83
0.038[a]	0.52	0.64	0.55
0.0256[b]	1.67	1.79	1.61
0.075	0.88	0.92	0.83
	1.2 moles/liter		
8.1	28.1	32.5	17.1
4.7	16.4	19.2	10.55
0.092	0.45	1.02	0.83
0.042	0.404	0.68	0.56
	0.7 mole/liter		
7.9	25	31.8	13.08
0.413	0.82	2.4	1.58
0.296	0.66	1.95	1.34
0.075	0.22	0.92	0.72
0.057	0.19	0.80	0.636
	0.3 mole/liter		
0.42	0.76	2.46	1.35
0.31	0.82	2.01	1.19
0.075	0.19	0.92	0.69
0.058	0.18	0.80	0.61

[a] Copolymerization temperature 25° C.

[b] Copolymerization in bulk at 25° C.

TABLE 3. Polymerization of Vinyl Chloride in the Presence of Various Amounts of Isobutyronitrile

Isobutyronitrile (mole)	0	0.0304	0.075	0.175	0.311	0.726
$\frac{\text{Isobutyronitrile}}{\text{Vinyl chloride}}$, (M/M)		0.087	0.227	0.59	0.95	2.3
$\overline{M}_n$ (osmometry)[a]	27,000	27,000	19,000	18,400	-	15,000
Yield after 6 hr, %	21	34	23	22	1.2	8.6

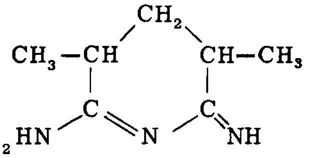
[a] Osmometry of solution in o-dichlorobenzene at 37° C.

amounts of isobutyronitrile. The results are reported in Table 3. A plot of $1/\overline{M}_n$ vs the ratio of concentrations of isobutyronitrile on monomer leads to an unaccurate determination of the transfer constant, which may be estimated to be about 10×10^{-4}. Such a value is very low compared to the above value of 5 for k_T/k_{cc}. It may also be noted that increasing the concentration of isobutyronitrile causes a retardation of polymerization.

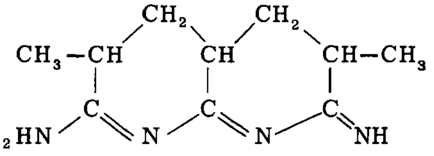
From these results and also from the previously mentioned result concerning the influence of dilution on kinetics it may be concluded that hydrogen transfer is not the major cause of the anomalous kinetics. Further investigations have been focused on the intramolecular copolymerization involving the C≡N triple bond.

SPECTROSCOPIC STUDIES

It has been observed visually that the copolymers are brown in color, with a maximum intensity for intermediate compositions. Coloration increases for the same composition with dilution of the monomer mixture. UV spectra have been obtained from DMF solution by using an Optica Model apparatus, a solution of polyacrylonitrile homopolymer prepared in bulk being placed in the reference cell. This solution shows a weak absorption with a maximum intensity at 270 nm, in agreement with the data of Patron [8]. Typical examples of spectra are shown in Figs. 6 and 7. Three maxima are clearly observed: the first one at about 270 nm is observed in all the samples and corresponds to the maximum observed in the acrylonitrile homopolymers. A second maximum at 290 nm is clearly more intense for intermediate compositions (60% acrylonitrile). The third one is chiefly observed for copolymers prepared in more dilute solutions and, at the same time, the second maximum tends to disappear. Absorptions at about the same positions (254 and 286 nm) have been observed by Takata et al. [11] for polycyclic model compounds obtained after ionic treatment of 2,4-dicyano-n-pentane and 2,4,6-tricyano-n-heptane to give, respectively:



and



The same authors have observed a third band at 320 nm in the heat-treated products of 2,4,6,8-tetracyano-n-nonane, and they propose

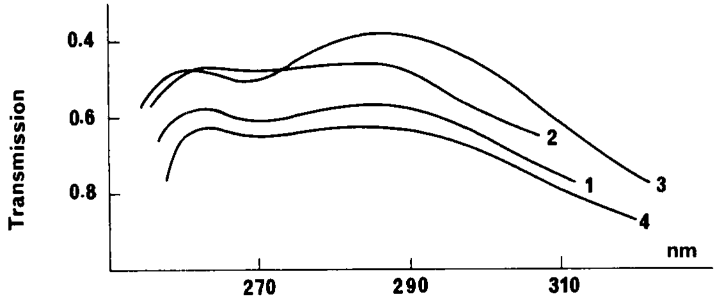


FIG. 6. Electronic spectra of vinyl chloride-acrylonitrile copolymer prepared with an initial overall monomer concentration of 2 moles/l. The concentration of the analysis DMF solution correspond to 1 mg of acrylonitrile units per milliliter of dimethylformamide. Effect of the copolymer composition (mole % of acrylonitrile unit): (1) 37%, (2) 45%, (3) 63%, and (4) 85%.

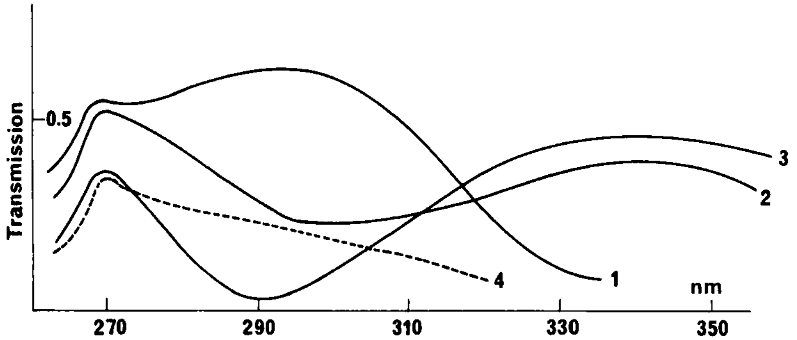
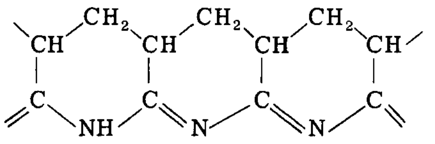
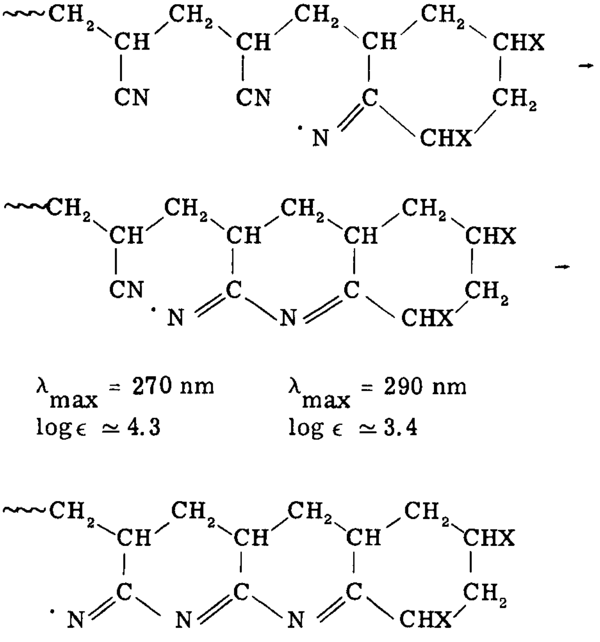


FIG. 7. Electronic spectra of vinyl chloride-acrylonitrile copolymers. Effect of the overall monomer concentration of the polymerization solution. (1) Copolymer with 45% mole % A units: concentration 2 moles/liter. (2) Copolymer with 42% mole % A units: concentration 1.2 moles/liter. (3) Copolymer with 55% mole % A units: concentration 0.7 mole/liter. (4) Copolymer with 43% mole % A units: bulk copolymerization.

that the absorption observed at 333 nm in the heat-treated polyacrylonitrile is due to sequences of three heterocycles:



Their results support the conclusion of Grassie and Hay [12] who have suggested that the thermal coloration of polyacrylonitrile, which has been shown [13] to be a radical process, is chiefly an intramolecular cyclization process. Thus it may be suggested that, after an intramolecular copolymerization process as suggested by Patron [8], the new radical may react with adjacent CN groups, leading to naphthyridinic or even polycyclic imine-type radicals.



λ_{max} = 270 nm λ_{max} = 290 nm

log ε ≃ 4.3 log ε ≃ 3.4

λ_{max} = 330 nm

It has been shown that further treatment of the copolymers in DMF under the polymerization conditions (several hours at 60°C) does not

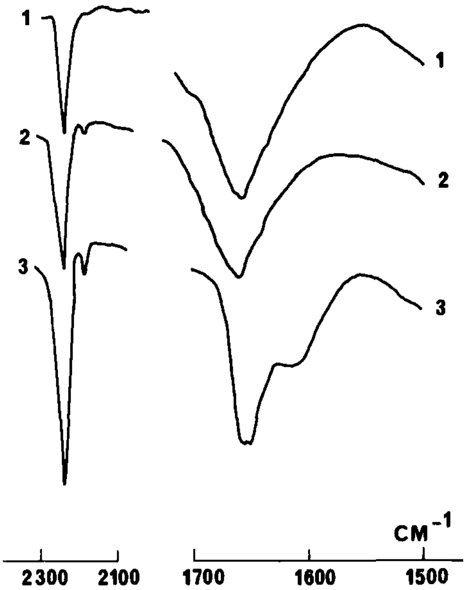


FIG. 8 IR spectra of acrylonitrile-vinyl chloride copolymers prepared in 2 monomer mole % concentrated DMF solutions (KBr disk: 10 mg/g). (1) Copolymer with 35 mole % A units. (2) Copolymer with 55 mole % A units. (3) Copolymer with 94 mole % A units.

change the UV spectra, so the formation of the structures causing the absorption is a part of the polymerization process and is not caused by ageing of the copolymers.

Thus an intramolecular polymerization process, involving the CN group, may be developed along the A sequences. The $C{=}N^{\cdot}$ radicals may undergo different reactions such as termination, transfer on DMF, or copolymerization with the monomers.

As compared with the spectra of acrylonitrile or vinyl chloride homopolymers, the IR spectra of the copolymers (Fig. 8) chiefly show three new bands at 1620 (always weak), 1660, and 2190 cm^{-1}. The first and last bands show a closely parallel behavior and are observed chiefly in the A rich copolymers; it is suggested that they correspond to the 270 nm absorption and are due to $>C{=}N^{\cdot}$ structures belonging to isolated cycles. The first band (1620 cm^{-1}) is present in the published spectra of heat-treated polyacrylonitrile but has not been discussed. The band at 2190 cm^{-1} has been attributed to α-β ethylenic nitriles [14] or to enaminonitriles [15]. The results reported in Table 4 also show the behavior of the band at 1660 cm^{-1} which is the

TABLE 4. Infrared Data on Homo- and Copolymers

% An copolymer	x = A/C (monomer feed)	{M} total	T (° C)	$\frac{D_{1660}}{D_{2240}}$	$\frac{D_{2190}}{D_{2240}}$
97.5	10.5	2.0	60	0.37	0.054
86.0	2.36	2.0	60	0.54	0.065
70.0	0.94	2.0	60	0.56	0.050
55.0	0.47	2.0	60	1.15	0.02
44.0	0.19	2.0	60	1.50	-
35.0	0.008	2.0	60	1.45	-
15.0	0.02	2.0	60	0.80	-
0	0	2.0	60	0.00	-
96.0	8.1	1.2	60	0.92	0.06
95.0	7.9	0.7	60	1.20	0.093
89.0	4.7	0.7	60	1.15	0.108
30.0	0.41	0.7	60	1.10	-
23.0	0.31	0.03	60	1.23	-
62.0	0.09	bulk	60	0.10	-
43.7	0.070	bulk	60	0.40	-
49.0	0.08	2.0	25	0.50	-

more intense; it increases with vinyl chloride content, with copolymerization temperature, and with dilution. This band is always mentioned in heat-treated polyacrylonitrile, and it may become very intense [12]. It is certainly to be associated with sequences of cyclic structures [11, 12]. In the present case its position may be influenced by chlorine in the first cycle, and its intensity may be occasionally influenced by traces of DMF strongly associated with the polymers even though several purification treatments have been carried out.

REACTION RATES AND MOLECULAR WEIGHTS

As a consequence of the intramolecular copolymerization reaction, a new radical based on a nitrogen atom is generated. As suggested by Patron [8], this new radical is not very reactive in propagation reactions

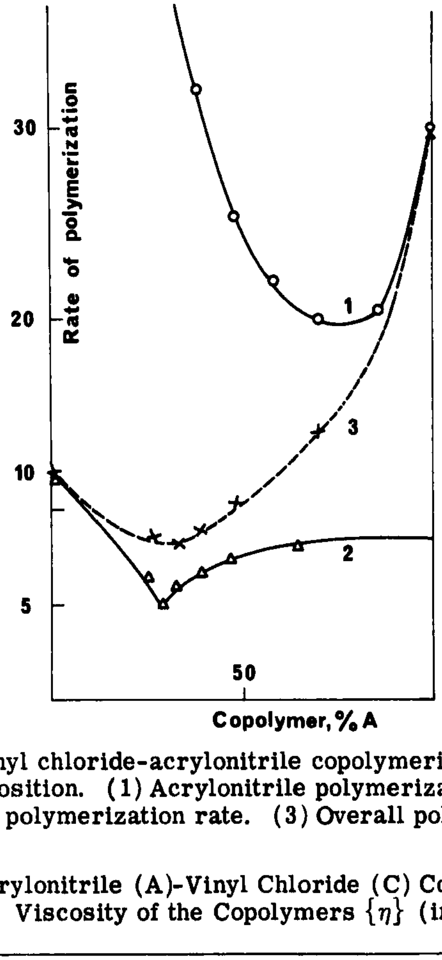


FIG. 9 Vinyl chloride-acrylonitrile copolymerization rate vs copolymer composition. (1) Acrylonitrile polymerization rate. (2) Vinyl chloride polymerization rate. (3) Overall polymerization rate.

TABLE 5. Acrylonitrile (A)-Vinyl Chloride (C) Copolymerization in DMF Solution. Viscosity of the Copolymers $\{\eta\}$ (in DMF at 25°C)

% A copolymer	94	69	41	37	15	0
$\{\eta\}$	54.4	40.0	17.2	8.2	12.5	40.4

and participate mostly in termination reactions. It results in a decrease of both reaction rates and molecular weight. These features have been confirmed experimentally, as shown in Fig. 9 and Table 5. The overall rate of copolymerization, as well as the individual polymerization rates for each monomer, which were directly obtained from chromatographic analysis, goes through a minimum. The initial decrease from the vinyl chloride rich side is accounted for satisfactorily by the well-known copolymerization retardation effect, and a continuous decrease down to the acrylonitrile homopolymerization rate is to be expected from the Lewis and Mayo theory. The minimum observed for both vinyl chloride and acrylonitrile consumption rates, as well as for the overall polymerization rate, may be explained by the presence of the new nitrogen-based radicals. These new radicals have low reactivity vs the propagation reaction but more easily undergo the termination reaction.

CONCLUSION

The hypothesis of an intramolecular copolymerization reaction involving the $-C{\equiv}N$ bonds of the acrylonitrile unit seems to be more feasible than that of a transfer reaction involving the α-hydrogen atom of the acrylonitrile unit. Formally, the kinetic scheme for the propagation reaction of both these mechanisms is the same. However, this scheme is not valid and has to be completed by taking into account the low reactivity of the new $-C{\equiv}N^{\cdot}$ radicals (noted $N^{\cdot}$) vs propagation. This means that the steady state equation for these new radicals must involve the termination reactions which are not negligible as compared with propagation reactions. The old equation

$$d[N^{\cdot}]/dt = 0 = k_I\,(ACC^{\cdot} + AAC^{\cdot}) - k_{NA}[N^{\cdot}][A] - k_{NC}[N^{\cdot}][C]$$

where k_I is the rate constant for the internal copolymerization reaction (assuming it is negligeable for A-ended radicals), has to be completed as

$$d[N^{\cdot}]/dt = 0 = k_I\,(ACC^{\cdot} + AAC^{\cdot}) - k_{NA}[N^{\cdot}][A] - k_{NC}[N^{\cdot}][C] - k_t[N^{\cdot}]\left\{[A^{\cdot}] + [C^{\cdot}] + [N^{\cdot}]\right\}$$

where k_t is a termination rate constant. In fact, the last term is an oversimplification because the termination rate constant may be dependent on the reactivity of each kind of radical.

Using this new equation the resolution of the new kinetic scheme is now possible and new data are to be obtained. Further experiments are in progress in our laboratory to obtain these new data from either the spin trapping technique applied to the copolymerization medium or the NMR analysis of the copolymers.

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