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Acrylonitrile Copolymerizations. VI. Influence of the Comonomer on the Intramolecular Cyclization Reaction

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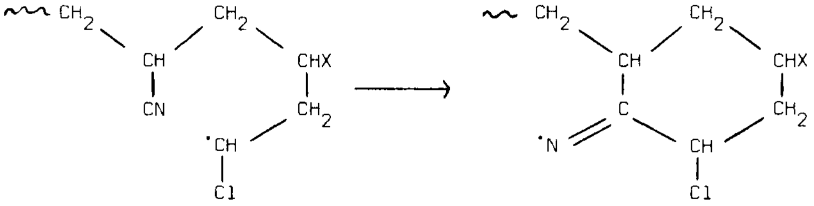
ABSTRACT

The intramolecular cyclization reaction involving the polymerization of cyano groups reported in a previous paper for the system acrylonitrile-vinyl chloride is studied for other comonomers with acrylonitrile including vinyl acetate, vinylidene chloride, butadiene, styrene, methyl acrylate, and methyl methacrylate. It is shown that the extent of the reaction is governed by the reactivity of the comonomer-unit ended radical, but the cyclization reaction cannot explain all the kinetic deviations observed.

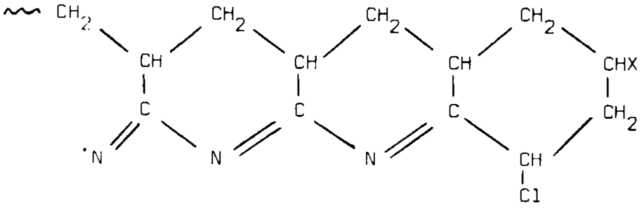
INTRODUCTION

In the preceding paper of this series [1] it was shown that the large deviations from the kinetic theory of copolymerization of Lewis and Mayo, observed in the case of vinyl chloride-acrylonitrile copolymerization might be satisfactorily interpreted, at least qualitatively, as being caused by the occurrence of an intramolecular cyclization reaction. This reaction involves the polymerization of a $-C{\equiv}N$ group carried by the antepenultimate unit from the growing radical following the attack of this radical.



where X is $-C{\equiv}N$ or Cl.

The reaction occurs to a smaller extent in the case of acrylonitrile homopolymerization [2], and this may explain the anomalous kinetic orders as being due to an enhancement of the termination reaction. Obviously the new radical (noted hereafter as N$^\cdot$) has a low reactivity toward the polymerization reaction and has a better chance to undergo a termination reaction. For that reason, in our previous studies of vinyl chloride-acrylonitrile copolymerization carried out in dimethylformamide (DMF) solution, it was observed that the overall and individual polymerization rates go through a minimum as a function of the feed composition, with a corresponding minimum of molecular weight. The extent of the cyclization reaction was shown to be enhanced by dilution and therefore the new N$^\cdot$ radical may cause propagation of the cyclization reaction by giving rise to polycyclic structures:



Otherwise, the reactivity of the N$^\cdot$ radical is very different from that of the vinyl chloride ended radical (noted C$^\cdot$), and can cause a relative decrease in the acrylonitrile consumption.

The purpose of the present paper is to examine the influence of the nature of the comonomer on the extent of the cyclization reaction. The latter may be estimated a priori in two ways: from a spectroscopic study of the colored copolymers and from the deviations observed kinetically.

The spectroscopic method gives only a relative estimate of the extent of the reaction. In the kinetic method it must be assumed that the cyclization reaction is the unique cause, or at least the major cause, of the kinetic deviations. A number of copolymer systems with acrylonitrile have been studied including vinylidene chloride, vinyl acetate, methyl acrylate, methyl methacrylate, styrene, and butadiene.

THE EXTENT OF THE CYCLIZATION REACTION

Kinetics

The cyclization reaction is to be considered as a deviation from the Lewis and Mayo theory. It causes changes in the expected polymerization rates, as well as in the copolymer composition. Calculation of the theoretical (Lewis and Mayo) polymerization rate requires knowledge of several constants: reactivity ratios, homopolymerization propagation and termination rate constants, and factor Φ for cross termination. For the copolymer composition, only the reactivity ratios are needed. Although the effect of the cyclization reaction is probably more pronounced on the polymerization rate than for the copolymer composition, we have chosen, for the sake of simplicity, to define the extent of the cyclization reaction from the composition. The procedure is as follows: the reactivity ratios are obtained from the extrapolation of the plots of n/x vs x or 1/x for low or large values of the monomer feed ratio x (ratio of the concentrations of monomers A and B), n being the corresponding copolymer composition ratio (dA/dB). Then the theoretical n is calculated from the Lewis and Mayo theory for any value of x. The extent of the cyclization reaction may be estimated from the value

$$\frac{\Delta n}{n} = \frac{n_{\text{exptl}} - n_{\text{calc}}}{n_{\text{calc}}}$$

Such plots are given in Figs. 1 and 2. Of course, such a procedure assumes that the cyclization reaction for acrylonitrile homopolymerization is negligible as compared to that occurring with copolymers.

Spectroscopy

In a previous paper [1] it was shown that the formation of cyclic and polycyclic structures causes coloration of the polymer. The UV-visible spectrum of polyacrylonitrile homopolymer shows a band at 270 nm with a tail toward the higher wavelength. In the case of the copolymer,

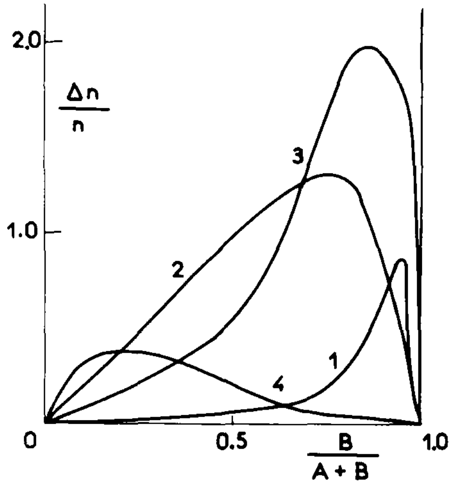


FIG. 1. Acrylonitrile (A) copolymerization. Deviation of composition from kinetic results. The comonomers (B) are vinyl acetate (1), vinyl chloride (2), butadiene (3), and styrene (4).

another band appears at 290 nm and, if the copolymerization has been carried out at a low monomer concentration, a third one at 330 nm. From the spectra of the model compounds prepared by Takata et al. [3], these new bands have been assigned to dicyclic and tri- (or poly-) cyclic structures, respectively. In the present study the optical density at 290 nm has been used as a spectroscopic measurement of the extent of the cyclization reaction. In these measurements the reference cell contains a solution of polyacrylonitrile adjusted so that the acrylonitrile units contents in both cells are the same. Examples of results are given in Fig. 3.

RESULTS: COPOLYMERIZATION KINETICS

A number of copolymerization experiments have been carried out at 60°C in DMF solution including vinyl acetate, vinylidene chloride, and methyl acrylate. The corresponding charge conditions and kinetic results (initial rates and copolymer composition) are given in Tables 1, 2, and 3, respectively. Using the copolymerization equation

$$n = \frac{dA}{dB} = \frac{1 + r_A x}{1 + r_B/x}$$

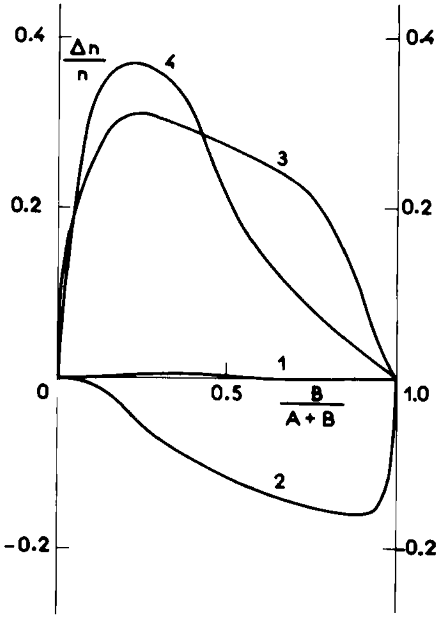


FIG. 2. Acrylonitrile (A) copolymerization. Deviation of composition from kinetic results. The comonomers (B) are vinylidene chloride (1), methyl acrylate (2), methyl methacrylate (3), and styrene (4).

where x = A/B and B is the comonomer concentration, plots of n/x vs x or 1/x for large and low values of x, respectively, permit the reactivity ratios r_A and r_B to be obtained. The values obtained are reported in Table 4, together with the corresponding literature data. This procedure has also been applied to other acrylonitrile copolymerization systems studied previously, including butadiene [4], styrene, and methyl methacrylate copolymers [5]. The agreement with the literature data is rather good in many cases, although the literature data are generally obtained from the medium composition range and our procedure enhances the influence of extreme composition copolymers. Large discrepancies are observed in the last two cases of Table 4: styrene and butadiene. It may be observed that these two monomers correspond to the largest differences in polarity with acrylonitrile, as shown from the difference $e_A - e_B$ of the e polarity factors of the Alfrey-Price Q,e scheme.

As shown in Figs. 1 and 2, the extent of the cyclization reaction, as

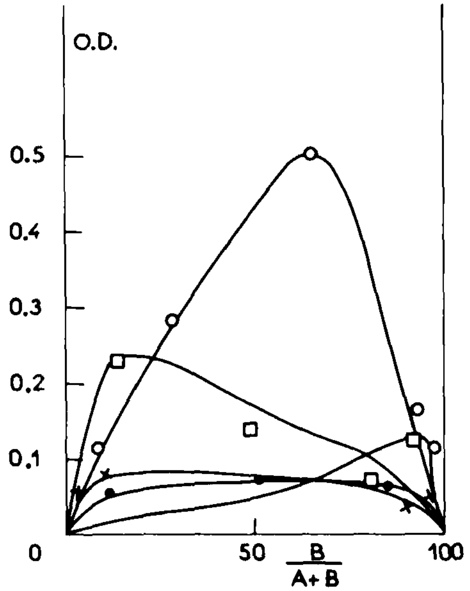


FIG. 3. Optical density at 290 nm vs copolymer composition for various acrylonitrile copolymers: vinyl chloride (○), butadiene (×), vinyl acetate (□), and vinylidene chloride (●).

defined by the kinetic method, may be very large, chiefly in the case of butadiene, vinyl chloride, vinyl acetate, and styrene. It is much more moderate in the case of methyl methacrylate and practically unnoticeable in the case of vinylidene chloride.

Surprisingly, the degree of deviation is changed in the case of methyl acrylate, but it remains limited.

The reasons for the difference in behavior of the various copolymers systems are not clear. Vinyl chloride and vinyl acetate radical are very reactive, and the cyclization reaction gives unreactive radicals, But vinylidene chloride radicals are also reactive radicals, while butadiene, styrene, and methyl methacrylate radicals are not very reactive. On the other hand, the 1,4-cis addition of butadiene leads to a conformation favorable for the cyclization reaction, but the 1,4-cis addition is a minor mode in this copolymerization [7]. In the other cases, styrene and methyl methacrylate, the steric hindrance certainly works against the cyclization reaction. For all these reasons, it seems difficult to explain the kinetic deviation from the Lewis and Mayo theory observed in many cases only on the basis of a unique secondary reaction such as cyclization.

TABLE 1. Charge and Initial Composition (n_A) in Acrylonitrile (A)-Vinyl Acetate (V) Copolymerization

A (moles)	V (moles)	DMF (moles)	$x_A = \frac{A}{V}$	$n_A = \frac{dA}{dV}$	$\frac{dp_A}{dt}$[a]	$\frac{dp_V}{dt}$[a]
1.02	0.018	6.07	52	211	0.16	0.039
0.907	0.038	6.07	22.3	89.7	0.15	0.038
1.17	0.100	6.11	11.60	46.4	0.16	0.039
0.94	0.145	5.77	6.51	29.6	0.155	0.034
0.538	0.480	5.71	1.12	6.95	0.160	0.026
0.240	0.780	5.70	0.310	1.85	0.185	0.031
0.160	0.840	5.60	0.192	1.200	0.200	0.032
0.067	0.858	5.62	0.078	0.690	0.300	0.034
0.028	0.870	5.63	0.0247	0.495	0.760	0.038
0.012	0.856	6.11	0.0128	0.400	1.22	0.0385

[a] Initial yield as A or V monomer conversion in percent per minute.

TABLE 2. Charge and Initial Composition (n_A) in Acrylonitrile (A)-Vinylidene Chloride (C) Copolymerization

A (mole)	C (mole)	DMF (moles)	$x_A = \frac{A}{C}$	$n_A = \frac{dA}{dC}$	$\frac{dp_A}{dt}$[a]	$\frac{dp_C}{dt}$[a]
0.68	0.04	5.04	13.0	12.8	0.165	0.21
0.97	0.13	4.96	7.45	6.95	0.092	0.10
0.70	0.34	5.44	2.08	1.80	0.036	0.042
0.48	0.55	4.88	0.875	0.97	0.045	0.040
0.34	0.77	5.10	0.437	0.56	0.066	0.052
0.28	0.856	5.70	0.33	0.50	0.048	0.032
0.16	0.92	4.95	0.174	0.26	0.075	0.050
0.10	0.93	4.95	0.11	0.126	0.057	0.047
0.05	0.995	4.87	0.051	0.092	0.140	0.078
0.02	1.18	4.68	0.018	0.026	0.165	0.117

[a] Initial yield as A or C monomer conversion in percent per minute.

TABLE 3. Charge and Initial Composition (n_A) in Acrylonitrile (A)-Methyl Acrylate (M) Copolymerization

A (mole)	M (mole)	DMF (moles)	$x_A = \frac{A}{M}$	$n_A = \frac{dA}{dM}$	$\frac{dp_A}{dt}$[a]	$\frac{dp_M}{dt}$[a]
0.755	0.018	6.25	42.0	45.8	0.147	0.134
0.728	0.031	5.74	23.3	24.0	0.161	0.156
0.836	0.078	5.74	10.7	11.0	0.176	0.172
0.70	0.207	6.20	3.38	3.7	0.275	0.257
0.223	0.761	6.0	0.292	0.395	0.46	0.34
0.56	0.713	5.98	0.079	0.110	0.49	0.35
0.027	0.531	5.70	0.051	0.069	0.54	0.39
0.026	0.68	5.65	0.038	0.044	0.52	0.46
0.014	0.76	5.82	0.018	0.019	0.69	0.64
0.011	0.916	6.35	0.012	0.014	0.69	0.61

[a] Initial yield as A or M monomer conversion in percent per minute.

TABLE 4. Reactivity Ratios

Comonomer B	r_A	r_B	Refs.	$e_A - e_B$[6]
Vinyl chloride	3.9	0.03	1	1.0
	3.28 ± 0.06	0.022 ± 0.02	6	
Vinyl acetate	4.0	0.008	This work	1.42
	4.05 ± 0.3	0.06 ± 0.013	6	
	6 ± 2	0.02 ± 0.02	6	
Vinylidene chloride	0.8	0.6	This work	0.84
	0.91 ± 0.1	0.37 ± 0.1		
Methyl acrylate	1.0	0.83	This work	0.60
	0.67 ± 0.1	1.26 ± 0.1	6	
Methyl methacrylate	0.4	1.0	5	0.80
	0.15 ± 0.07	1.20 ± 0.14	6	
Butadiene	0.07	0.03	4	2.25
	0.40 ± 0.02	0.04 ± 0.01	6	
Styrene	0.29	0.30	5	2.0
	0.04 ± 0.04	0.40 ± 0.5	6	

RESULTS: COPOLYMER SPECTRA

The most interesting results of the spectroscopic study are illustrated in Fig. 3. The more intensive colorations are again observed with vinyl chloride copolymers, but the maximum of optical density is located at a composition somewhat different from that of the maximum of Δn/n (Fig. 1). The discrepancy between the spectroscopic data and the kinetics is even more pronounced for vinyl acetate copolymers where the two maxima are located at the two extreme parts of the composition range. It may also be noted that the optical density at 290 nm of butadiene copolymer remains moderate although the kinetic deviation Δn/n is very large for butadiene-rich copolymers. In the reverse sense, there are no kinetic deviations in the case of vinylidene chloride but the optical density is as large as that observed with styrene copolymers. It may therefore be concluded that there are no correlations between the absorption at 290 nm and the composition deviations calculated from kinetic results, except perhaps in the case of vinyl chloride copolymers.

CONCLUSIONS

The anomalous kinetics might be the result of many reasons, possibly of chemical as well as of physical origin, so it will be very difficult to define these reasons if several of them are concerned in the same copolymerization. The coloration is probably directly related to a specific chemical secondary reaction such as the cyclization reaction. The latter has a general character and may be observed even with acrylonitrile homopolymers; it is undoubtedly enhanced in a copolymerization, and the spectroscopic study shows in this connection that it is very dependent upon the reactivity of the comonomer radicals. However, because there is a competition between that reaction and the propagation reaction, others factors are probably involved such as the coiling of the macromolecules in solution. For instance, the differences observed between the vinyl chloride and vinyl acetate copolymers can be explained by other factors than their reactivities or sequence distributions which are very similar.

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