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Acrylonitrile Copolymerization. VIII. Radical Determination by the Spin-Trapping Technique

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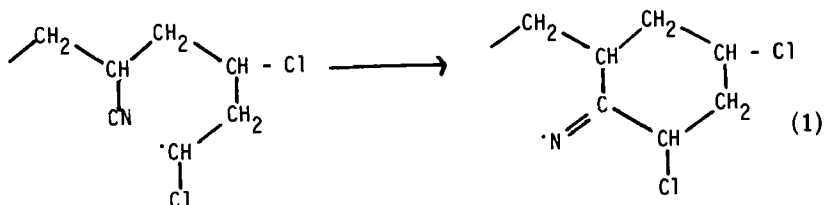
ABSTRACT

The technique of spin trapping of polymer radicals by 2-methyl-2-nitrosopropane has been applied to the study of acrylonitrile copolymerization. Provided the concentration of the spin trapping agent is kept low, and the samples are kept at low temperature during storage before obtaining the ESR spectra, quantitative studies of styrene-acrylonitrile copolymerization are possible. However, the spin-trapping reaction is a competitive one, and the trapping efficiency is dependent on the reactivity of the radicals present. In the case of acrylonitrile copolymerization with either vinyl chloride or vinyl acetate, these two last radicals are trapped preferentially. Furthermore, the cyclization reaction observed with many acrylonitrile copolymerization is nearly eliminated in the presence of the spin-trapping agent.

INTRODUCTION

In previous papers of this series [1, 2], it has been shown that in many cases, the behavior of the radical copolymerization involving acrylonitrile is different from that expected on the basis of radical copolymerization theory. More precisely, it seems that when the

comonomer gives rise to active radicals, for instance vinyl chloride or vinyl acetate, a cyclization reaction takes place, involving the attack of the $C\equiv N$ group by the growing radical, according to the scheme (1).



Being relatively unreactive, the new imine radical reacts preferentially in termination reactions rather than in propagation [1]. The cyclization reaction, however, is important only in a few cases, and other events, possibly of physical nature (association with solvents, preferential solvation) may be involved, for instance in the case of styrene [2].

In order to get more information about the nature of this phenomenon, a study of the radicals might be of interest. It has been already suggested that the reactivity of radicals may be influenced by associations with solvents or reactants [3]. The study of radicals is chiefly done by use of ESR spectroscopy. A flow technique involving use of a redox system to increase the actual concentration of radicals up to the measurement level, has been applied by several authors to the study of the polymerization [4, 5], but, owing to the enormous concentration of radicals generated in these experiments, the results are chiefly related to the initiation reaction and little information is obtained about the propagation reaction. Further, the technique was limited to water-soluble systems. Recently, Russian scientists, using an improved ESR apparatus, have been able to study the propagation radicals in a few cases: styrene [6], methyl methacrylate, and vinyl acetate [7]. Their technique, which is not readily available, has not been yet applied to copolymerization. We preferred to use indirect ways.

A first approach has been described recently [8]. It is based on kinetic data obtained from the determination of the consumption rate of each monomer; then, assuming the reactivity ratios and the homopolymerization rate constants are known, it is possible to derive the actual concentration of each kind of radical. Application of this method to styrene-methacrylate and to vinyl chloride-vinyl acetate

copolymerization gives a good agreement with the copolymerization theory. Anomalous behavior is observed for the systems involving acrylonitrile copolymerized with either vinyl chloride or vinyl acetate.

A more direct approach is possible by use of the so-called "spin-trapping" technique: by reacting the radicals to be studied with suitable nitrones or nitroso compounds, one gets stable nitroxide radicals which may be identified and quantitatively studied by ESR. The method has been extensively used in organic chemistry [9]. In polymer chemistry, earlier results concerning radical polymerization of styrene were obtained by Chalfont et al. [10]. The first data on copolymerization have been more recently published by Japanese scientists [11]. They observed a number of secondary reactions leading to ESR signals not related to the propagating radicals and noted large differences in intensity between the signals of the polymerization solution and of the precipitated polymers. These differences show that the polymeric nitroxide radicals are not stable. From these results, arguing that the spin-trapping yield may be largely dependent on the nature of the trapped radicals, they concluded that it was not possible to derive any quantitative data from the spin trapping in copolymerization. Our work lead to a rather more satisfying conclusion, after optimal conditions to be used had been ascertained in a preliminary study.

PRELIMINARY STUDY

Polymerization of methyl methacrylate in toluene solution at 60°C, initiated by azobisisobutyronitrile (AIBN) was carried out. 2-Methyl-2-nitrosopropane (tBuNO) was used as spin-trapping agent. The reaction was followed by taking aliquots at various time intervals. The polymerization kinetics were followed through gas-chromatographic analysis as usual in our laboratory. ESR measurements were carried out with a Varian ESR 4502 instrument, either on the polymerization solutions or on the polymers after precipitation and vacuum drying. Comparison of the intensity of these signals may be obtained by using external diphenylpicrylhydrazyl radical. The polymerization solutions were carefully shielded from any irradiation in order to avoid spin trapping of the radicals produced by decomposition of tBuNO.

The results are illustrated in Fig. 1. Because the nitroso compounds are powerful inhibitors [12], no polymer is formed at the beginning of the experiment. Polymerization takes place with an increasing rate, as soon as the concentration of tBuNO has been decreased enough, and then goes to a normal rate. A rather large signal of three lines is

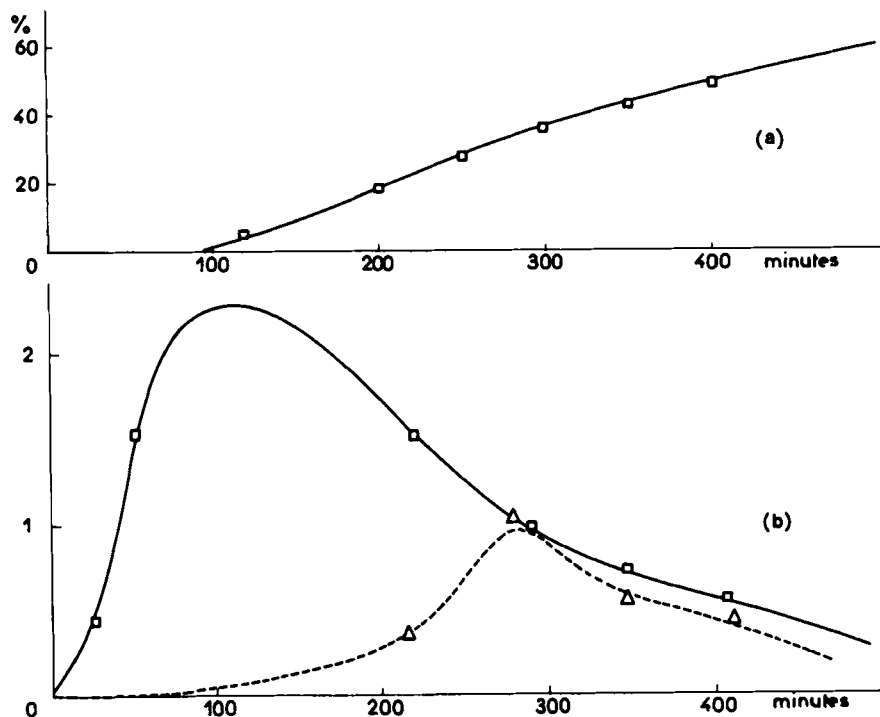
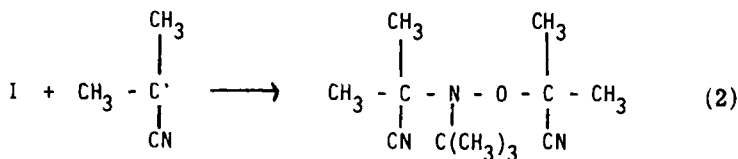
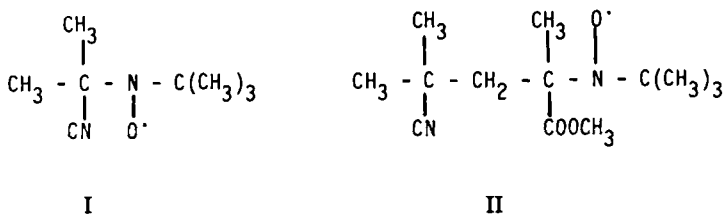


FIG. 1. Plots of (a) monomer conversion vs. time and (b) intensity of the ESR signal of (\square) reaction medium or (\triangle) polymers after precipitation for polymerization of methyl methacrylate (2.19 mole/liter) in toluene solution at 60°C initiated by AIBN (1.9×10^{-2} mole/liter) in the presence of tBuNO (1×10^{-3} mole/liter). Arbitrary units: comparison with the intensity of a DPPH signal.

obtained from the polymerization solution after a few minutes and before any trace of polymer can be observed. That signal goes through a maximum, observed incidentally at the beginning of the polymerization, and decreases slowly. The corresponding nitroxide radical may be attributed either to a primary radical (I) or more probably to a just-initiated polymerization radical (II). These radicals are probably not stable and may be coupled with other primary radicals [Eq. (2)].

The signal from precipitated polymer is also a three-line signal, as expected, with the same coupling constants. Its intensity is initially



much lower than the signal of the solution. It also increases, goes through a maximum, and then decreases. The maximum is observed approximately at the point of the maximum polymerization rate; at that point and thereafter, it is approximately as intense as the signal of the solution. It may be concluded therefrom that, after this second maximum, when the concentration of the spin trapping agent is low enough, chiefly the growing polymer radicals are trapped.

Our observations are in good agreement with the earlier results of Chalfont [10], who showed that only the polymer signal is obtained when the concentration of nitroso compounds is low enough (1×10^{-3} mole/liter in the case of styrene). It may be suspected that the difficulties encountered by the Japanese authors [11] are due chiefly to the rather high concentrations they used (2×10^{-2} mole/liter). Other observations showed that the reaction of tBuNO with monomers, according to the mechanism proposed by Túdós et al. [12] is important only in the case of methyl methacrylate or methyl acrylate but may be considered negligible in the case of styrene, acrylonitrile, vinyl chloride, and vinylidene chloride. Finally, it has been observed that most of the signals observed are not stable with time, even if one uses the precipitated polymers.

Experiments were therefore carried out with very low concentrations of tBuNO ($1-7 \times 10^{-3}$ mole/liter), and the ESR measurements were performed as soon as possible (less than 10 min) after the sampling, the sample being kept at -30°C before performing the measurement at 20°C .

STYRENE-ACRYLONITRILE COPOLYMERIZATION

Figure 2 illustrates the ESR spectra obtained from the solution homopolymerization of styrene and acrylonitrile. In both cases, the spectra show mainly six lines, as expected from the splitting of the three nitroxide main lines by the proton of the polymer radical. The coupling constant obtained from either the nitrogen or the proton are given in Table 1 and compared with the literature values. Nearly identical spectra have been obtained after precipitation in the case of polystyrene.

In the case of copolymerization, a few spectra are illustrated in Fig. 3. The progressive change means that both radicals are actually trapped. A quantitative titration has been done; owing to the rather

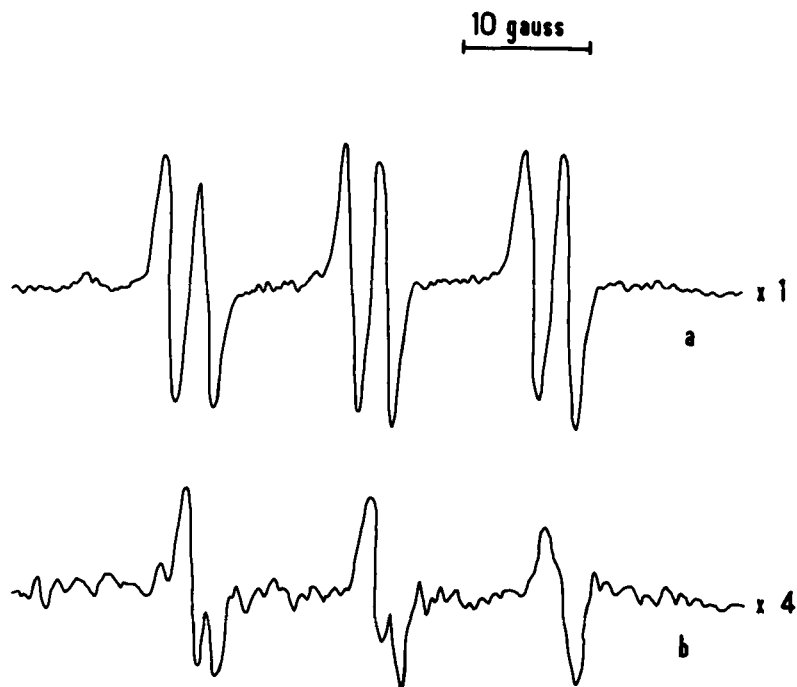


FIG. 2. ESR spectra of homopolymerization of (a) styrene or (b) acrylonitrile in DMF solution at 60°C after 30 min. Concentrations: monomer, 4 mole/liter; AIBN, 4×10^{-2} mole/liter; tBuNO, 4×10^{-3} mole/liter.

TABLE 1. Coupling Constants from ESR Spectra of Homopolymerization Solutions

Polymer	Nitrogen coupling constant α_N (gauss)		Hydrogen coupling constant α_H (gauss)	
	This work	Literature ^a	This work	Literature ^a
Polystyrene	14.70	15.30	3.0	3.05
Polystyrene ^b	14.30	14.90		
Polyacrylonitrile	15.25	14.90	1.50	2.58
Poly(vinyl chloride)	15.20		2.5 ^c	
Poly(vinyl acetate)	12.50	12.60	1.75	1.81

^aData of Kunitake and Murakami [11].

^bDetermined from the ESR spectrum of the separated polymer in toluene.

^cChlorine coupling constant.

poor precision of the coupling constants, the simulation of the spectra was not carried out. A more simple method has been chosen. It may be observed from Fig. 3 that one of the two central lines is always higher than the second. The reason is that this high central line is the sum of the contribution of styrene and acrylonitrile radicals while the lower central line is due to styrene radicals only because of the difference of coupling constants. On this basis, from the ratios of the height of these two lines, the ratio of acrylonitrile to styrene radicals (A'/S') may be calculated. From known mixtures of homopolymerization solutions, a calibration curve has been drawn and used to get the ratio A'/S' in the copolymerization solution. The results are illustrated in Fig. 4. The experimental points are compared with both the curve calculated from the reactivity ratios and homopolymerization rate constants and the experimental points from the kinetic method obtained by gas chromatographic analysis of the monomer mixture, as described in a previous paper [8]. The agreement is quite good.

It may be concluded that in the styrene-acrylonitrile radical copolymerization the concentrations of each of the two radicals are quite normal. There is no indication for the presence of imine-type radicals which might appear after a cyclization reaction. This result is not unexpected, because these copolymers are never highly colored.

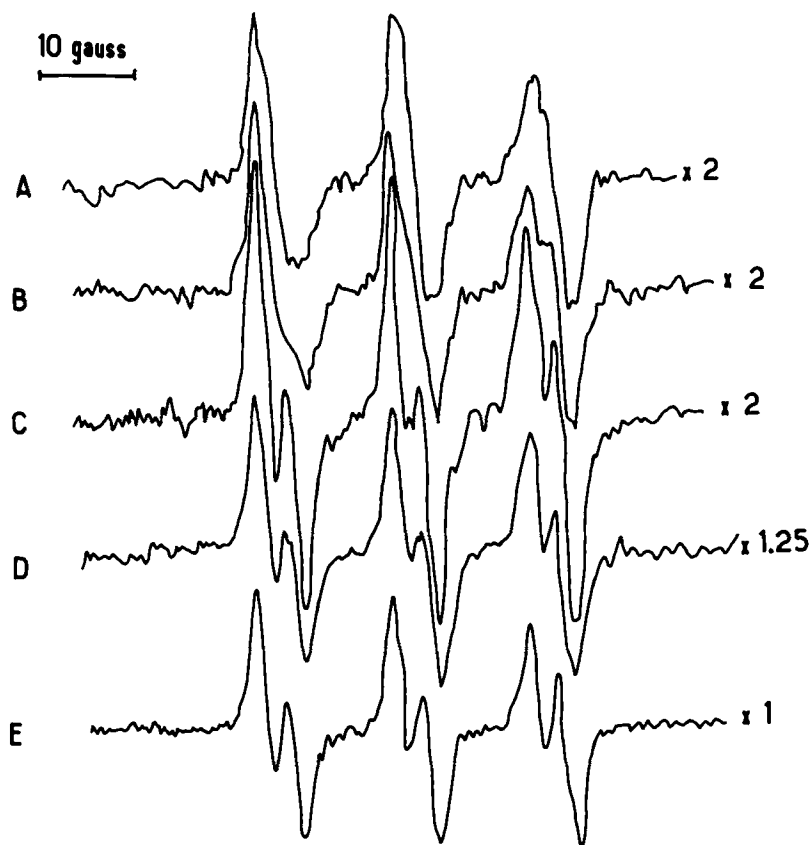


FIG. 3. ESR spectra of styrene-acrylonitrile copolymerization in DMF solution at 60°C after 30 min for different values of $x_{AN} = (AN)/(S)$: (A) 6.8; (B) 1.8; (C) 0.8; (D) 0.37; (E) 0.156. Concentrations: monomer 2 mole/liter; AIBN, 4×10^{-2} mole/liter; tBuNO, 7.5×10^{-3} mole/liter.

VINYL CHLORIDE-ACRYLONITRILE COPOLYMERS

Figure 5 shows an ESR spectrum of vinyl chloride homopolymerization after spin trapping by tBuNO. It must be noted that such a spectrum is not stable. It must be taken immediately after sampling and the polymerization time must be less than about 30 min. Otherwise

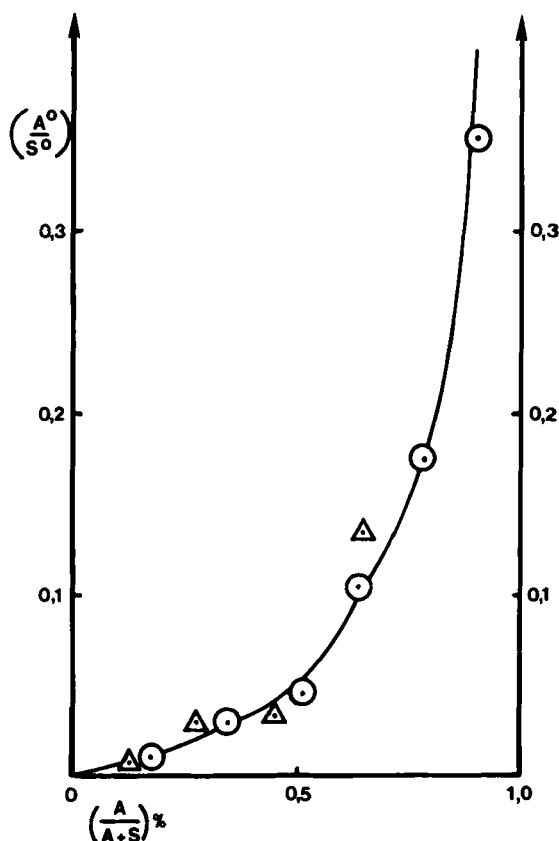


FIG. 4. Ratio of acrylonitrile to styrene radicals as a function of the monomer composition: (—) calculated curve; (o) experimental points from the kinetic method by gas chromatographic analysis; (Δ) experimental values from ESR spectra after spin trapping by tBuNO.

the signal is progressively replaced by a degenerate three-line signal. Poly(vinyl chloride) radicals after trapping show a 24-line signal, owing to the splitting by the α -proton at first and also the chlorine atom (spin 3/2). The observed coupling constants are reported in Table 1; to our knowledge there are no corresponding values in the literature.

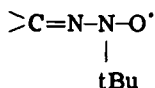
The spectra obtained for some vinyl chloride-acrylonitrile copolymerizations are illustrated in Fig. 6. They show that the



FIG. 5. ESR spectrum of vinyl chloride homopolymerization in DMF solution at 60°C after 23 min. Concentrations: monomer, 1.5 mole/liter; AIBN, 1.5×10^{-2} mole/liter; tBuNO, 3×10^{-3} mole/liter.

contribution of the vinyl chloride radical remains important for rather low concentrations of vinyl chloride, although from the reactivity ratios ($r_{AN} = 4$ and $r_{VC} = 0.03$ [15]) the amount of these radicals

has to decrease very much with increasing concentration of acrylonitrile. The reason for this is probably a preferential trapping of vinyl chloride radicals by tBuNO owing to their higher reactivity compared to that of acrylonitrile radicals. It may be mentioned here that the same situation has been observed in the case of styrene-vinyl chloride copolymerization, although the expected ratio of vinyl chloride to styrene radical concentrations would be about 10^{-4} . There is again no indication of imine radicals which, upon trapping, are expected to give a nine-line signal upon splitting of the nitroxide signal by the nitrogen atom of the imine radical III.



III

Of course, this nine-line signal may be obscured by the 24-line signal of the trapped vinyl chloride radicals. However, it has been

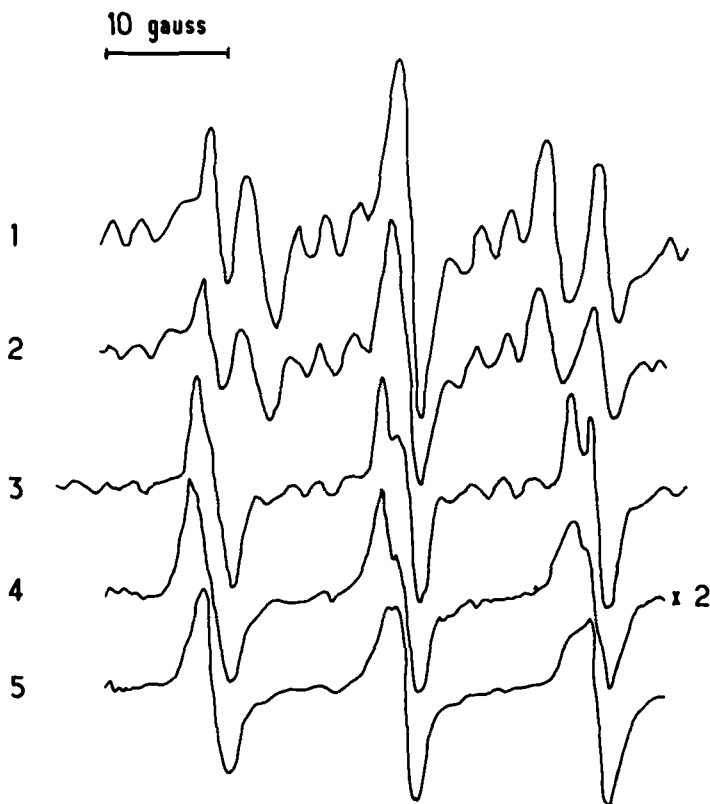


FIG. 6. ESR spectra of acrylonitrile-vinyl chloride homopolymerization and copolymerization in DMF solution at 60°C after 25 min: (1) vinyl chloride homopolymerization; (5) acrylonitrile homopolymerization; copolymerization at $x_{VC} = (VC)/(AN)$: of (2) 9, (3) 3, or (4) 0.33. Concentrations: monomer, 1.5 mole/liter; AIBN, 1.5×10^{-2} mole/liter; tBuNO, 3×10^{-3} mole/liter.

observed that, when the copolymerization is carried out in the presence of tBuNO, the coloration of the copolymer is lower. Typical results are illustrated by the electronic spectra of two copolymers of the same composition (Fig. 7). It is obvious that the spin-trapping reaction competes successively with the cyclization reaction responsible for the coloration.

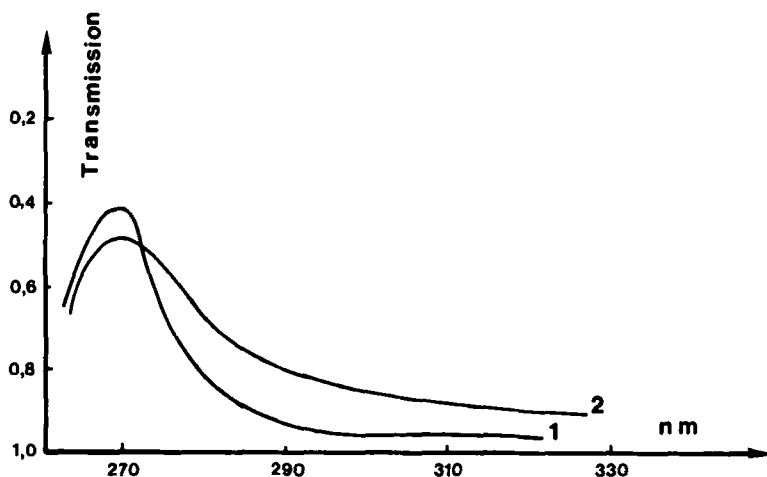


FIG. 7. Electronic spectra of vinyl chloride-acrylonitrile copolymers (55% AN) prepared in DMF solution (monomer, 0.7 mole/liter) at 60°C: (1) in the presence of *t*BuNO; (2) in the absence of *t*BuNO.

VINYL ACETATE-ACRYLONITRILE COPOLYMERIZATION

A few ESR spectra of samples obtained during the polymerization of vinyl acetate and its copolymerization with acrylonitrile in the presence of *t*BuNO are illustrated in Fig. 8. The spectrum of the spin-trapped vinyl acetate is a poorly resolved signal showing six main lines. The corresponding coupling constants are reported in Table 1.

When the acrylonitrile concentration increases, the spectrum is not very much changed although one may expect a higher concentration of acrylonitrile radicals. The main reason is probably the same as in the previous case. However, the coupling constants of the two kinds of signal are not very different.

It is obvious that a secondary signal appears in all the spectra. Obviously, it cannot be attributed to the imine radical because it is already observed in the spectrum of vinyl acetate homopolymerization (curve 1, Fig. 8). Such a signal might arise from methylene-ended radicals (9 lines after trapping) produced by transfer reaction upon the CH_3 groups of the monomer or of the polymer. Transfer to

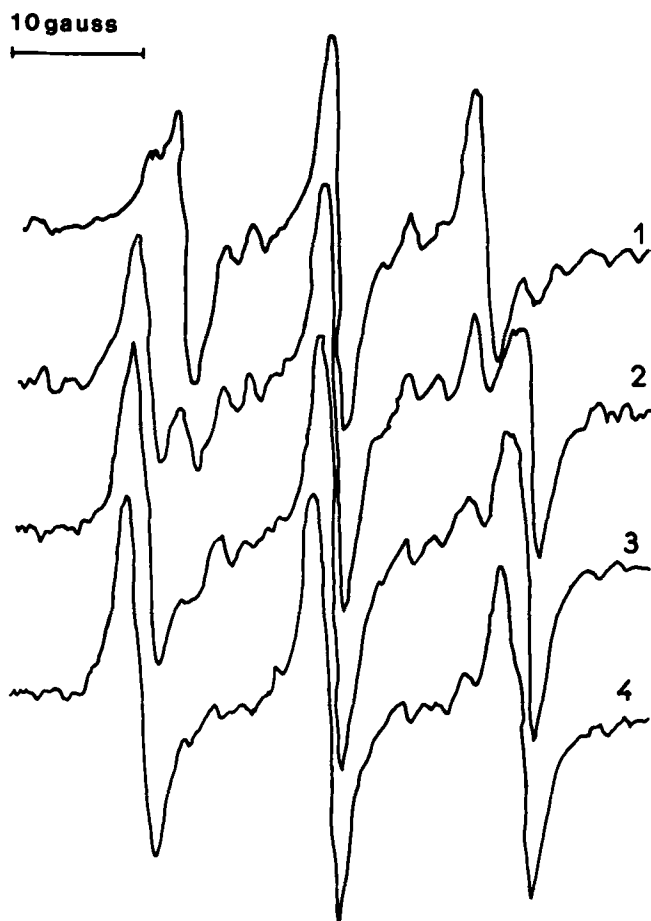


FIG. 8. ESR spectra of vinyl acetate-acrylonitrile copolymerization in DMF solution at 60°C after 30 min: (1) vinyl acetate homopolymer; and copolymers with $x_{VA} = (VA)/(AN)$ of (2) 19, (3) 3, or (4) 1. Concentrations: monomer, 0.7 mole/liter; AIBN, 1×10^{-3} mole/liter; $t\text{BuNO}$, 2×10^{-4} mole/liter.

methyl groups of the monomer have been already observed by Kunitake and Murakami [14] with methyl methacrylate, methacrylic acid, α -methylstyrene, and methacrylonitrile. Transfer to methyl groups of poly(vinyl acetate) has been already observed by Melville [16], although more recently, Japanese authors [17] have shown that such transfer was less frequent than transfer to the α -hydrogen atom of the poly(vinyl acetate) unit.

CONCLUSION

A quantitative study of the styrene-acrylonitrile copolymerization has been successfully carried out by the spin-trapping technique.

The success of the method is probably due to the fact that the two radicals have about the same reactivity and also that the two trapped radicals are rather stable.

With vinyl chloride or vinyl acetate copolymerization, these two conditions are not fulfilled, and the most reactive radicals are trapped preferentially even if their relative concentrations are quite small. Further, the trapped radicals are not stable at all and are progressively replaced by more stable radicals, probably from transfer reaction to the trapping agent itself. The lack of stability of the trapped poly(methyl methacrylate) radicals may explain also why the Japanese authors [11] did not get good results in the study of copolymerization with this monomer. We have indeed confirmed these poor results in the case of styrene-methyl methacrylate copolymers [18].

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