less soluble. After each precipitation, the polymer was dried at 40 °C (1 mm) in a vacuum oven. Any unreacted methyl methacrylate would be removed in the drying process. The copolymer was considered pure when the absorption bands for olefinic linkages found in the methyl *α*-*n*-alkylacrylate had disappeared from its infrared spectrum.

(E) Identification of the Copolymers. Copolymers were identified through infrared spectroscopy[9] and elemental analyses (Tables I and II). Infrared spectra showed that the absorption bands for olefinic linkages at 1631 (vinyl CO) and 937 cm^{-1} (R—C[C(=O)—]=CH$_2$) found in the spectra of the methyl *α*-*n*-alkylacrylates (alkyl = $C_{16}H_{33}$ and $C_{18}H_{37}$) had disappeared in each of the copolymers. There was a slight shift of the absorption band at 1730 cm^{-1} (characteristic of *α*,*β*-unsaturated esters) to 1739 cm^{-1} (characteristic of saturated esters). There was a band at 720 cm^{-1} ($(CH_2)_n{}^-$, $n \geq 4$) indicating the presence of a long alkyl chain, which would also be present in the monomer. Copolymer composition was calculated on the basis of the average carbon content in the copolymer in duplicate analyses.

(F) Homopolymerizations. Methyl *α*-*n*-alkylacrylates and methyl methacrylate were homopolymerized using free-radical (AIBN) and anionic (sodium) catalysts. In the free-radical catalyzed polymerizations, the reaction mixtures were as follows: 3 mM methyl *α*-*n*-alkylacrylate, 0.001 mM AIBN; 6 mM methyl methacrylate, 0.002 mM AIBN. The anionic polymerization reaction mixtures were as follows: 3 mM methyl *α*-*n*-alkylacrylate, 0.16 mM sodium, 1 mL of toluene; 6 mM methyl methacrylate, 0.23 mM sodium, 0.9 mL of toluene. The polymers were isolated, purified, and identified in the same manner as the copolymers.

References and Notes

(1) A patent has been granted covering the free-radical initiated copolymerizations. H. Gisser and H. E. Mertwoy. U.S. Patent 3 972 864 (1976). A patent covering the sodium-initiated polymerizations is pending.

(2) Presented before the Division of Polymer Chemistry at the 10th Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 1976.

(3) H. Gisser and H. E. Mertwoy, *Macromolecules*, **7**, 431 (1974); U.S. Patent 3 687 922 (1972).

(4) K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, **81**, 198 (1965).

(5) M. Iwama, H. Utiyama, and M. Kurata, *J. Macromol. Chem.*, **1**, 701 (1966).

(6) N. V. deBataafsche, German Patent 73 429 (1953).

(7) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers", Interscience, New York, N.Y., 1967, p 377.

(8) K. Chikanishi and T. Tsuruta, *Makromol. Chem.*, **81**, 211 (1965).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, N.Y., 1960, pp 34–53.

ESR Studies of Copolymerization of Crotonic Compounds with Acrylonitrile

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ABSTRACT: Copolymerization of 1,2-disubstituted vinylmonomers with acrylonitrile (AN) was studied by electron spin resonance. Using a rapid-flow mixing system the initial stages in the copolymerization of crotonic acid (CAC), crotonitrile (CNI), crotonaldehyde (CAD), and the ethyl ester of crotonic acid (CAEt) with acrylonitrile were studied in aqueous solution. The head-to-tail ratio of the formed monomer radicals follows the order CAEt ≈ CAC > CNI > CAD. The relative reactivities of the head and tail radicals toward AN correlate well with resonance and inductive effects in the monomers. The overall reactivity of the monomer radicals toward AN follows the order CAD > CAC > CAEt > CNI.

In previous studies of radical polymerization in our laboratory, using the ESR technique, the homopolymerization of monomers like vinyl esters, butadiene, trimethylolpropane monoallyl ether has been investigated.[1-3] Copolymerization of vinyl esters with various monomers[4,5] and copolymerization of water-soluble monomers like vinyl sulfonate and allyl sulfonate with acrylonitrile[7] have also been investigated. Reactions of 1,2-substituted vinyl monomers, i.e., crotonic compounds, when attacked by free-radical initiators were investigated by Izumi and Rånby.[6]

Electron spin resonance combined with a rapid flow mixing system is a powerful method for investigating the reactions in free-radical polymerizations. Particularly for copolymerizations this method has given good results. Conventionally, reactivity ratios in copolymerization are derived from the overall composition of the copolymers formed. This gives only a statistical picture of the system. With ESR studies it is possible to measure directly radical reactivities toward monomers.

In this study we present results obtained for copolymerization of four 1,2-substituted vinyl monomers (crotonic compounds) with acrylonitrile. The monomers studied are crotonic acid, crotonitrile, croton aldehyde, and ethyl crotonate (the ethyl ester of crotonic acid).

From ESR data the relative reactivities of the different monomer radicals to acrylonitrile monomer were derived and compared with reactivity ratios calculated from *Q*,*e* values from the literature. Furthermore, information about the conformation of the radicals was obtained from the ESR spectra.

Experimental Section

The ESR spectra were observed using a flow system[8-10] with a rapid-flow mixing cell[11] inserted into a TE 011 mode cylindrical cavity of a JES-ME-1X spectrometer from JEOL Ltd., Tokyo.

The flow rate used was 7.5 mL/s unless otherwise stated. This flow rate corresponds to a time lag from mixing to the center of the cavity of 0.018 s. The polymerization was initiated by hydroxyl radicals formed in a redox reaction between aqueous hydrogen peroxide (0.22 mol/L) in one of the solutions and aqueous titanium trichloride (0.016 mol/L) in the other. The pH was adjusted to 1.4 by adding sulfuric acid. The monomer concentrations used were in the range 0.005–0.07 mol/L. All measurements were made at room temperature (22 ± 2 °C).

The ESR signal was recorded as the first derivative of the microwave absorption vs. the magnetic field. Radical concentration was taken as proportional to signal amplitude times the square of the signal width. The magnetic field was calibrated with an Mn^{2+} sample. The following reagents were used: 15% titanium trichloride in water (Riedel-de Haen, Hannover), 30% hydrogen peroxide in water, concentrated sulfuric acid, acrylonitrile (AN), crotonic acid (CAC), croton aldehyde (CAD), ethyl crotonate (CAEt) (all from E. Merck AG, Darmstadt), and crotonitrile (CNI) (Merck-Schuchardt).

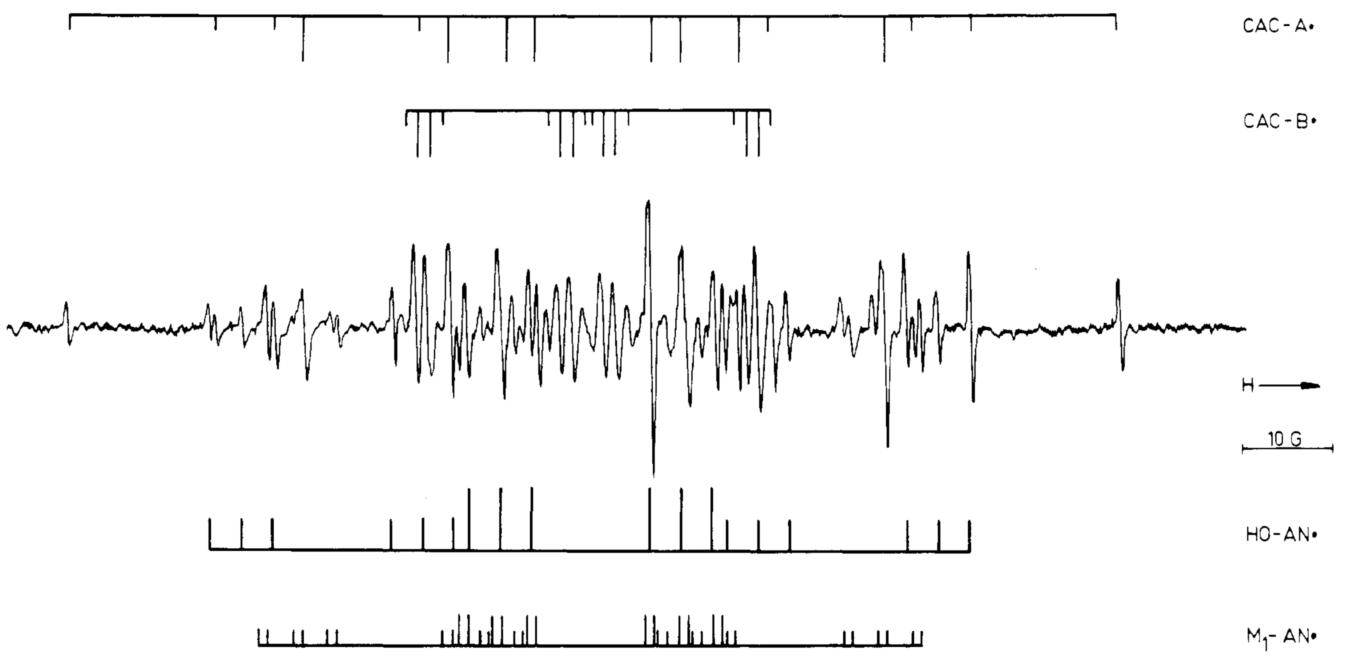
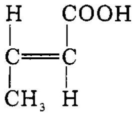
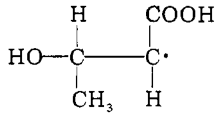
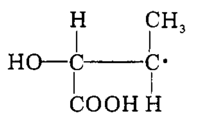
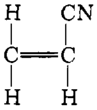
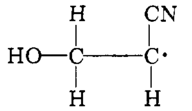
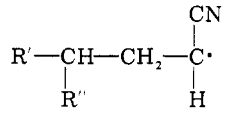


Figure 1. ESR spectrum from the copolymerizing system crotonic acid (CAC)/acrylonitrile (AN) initiated with the redox system H_2O_2–Ti^{3+}: [CAC] = 0.055 mol/L, [AN] = 0.020 mol/L.

Table I
Free Radicals Formed in the Copolymerizing System CAC/AN[a]

Monomer	Radical formed	Designation
 $\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}=\overset{\text{COOH}}{\underset{\text{H}}{\text{C}}}$	 $\text{HO}-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\overset{\text{COOH}}{\underset{\text{H}}{\text{C}}}\cdot$	CAC-B•
	 $\text{HO}-\overset{\text{H}}{\underset{\text{COOH}}{\text{C}}}-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\cdot$	CAC-A•
 $\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\overset{\text{CN}}{\underset{\text{H}}{\text{C}}}$	 $\text{HO}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{CN}}{\underset{\text{H}}{\text{C}}}\cdot$	HO-AN•
	 $\text{R}'-\underset{\text{R}''}{\text{CH}}-\text{CH}_2-\overset{\text{CN}}{\underset{\text{H}}{\text{C}}}\cdot$	M$_1$-AN•

[a] An "A radical" is formed from a crotonic compound by radical addition to the monomer tail and a "B radical" by addition to the monomer head.

Results

Series of ESR spectra for the systems CAC/AN, CNI/AN, CAD/AN, and CAEt/AN were recorded with the concentration of the crotonic compound constant at 0.055 mol/L. The acrylonitrile concentration was varied from 0.005 to 0.07 mol/L. In all cases well-resolved spectra were obtained and interpreted.

The Monomer System CAC/AN. Figure 1 shows the ESR spectrum of the copolymerizing system CAC/AN. In this spectrum four components can be observed. Two of them are due to radicals formed by addition of HO• to CAC, CAC–A•, and CAC–B• (see Table I), one is due to AN monomer radical, HO-AN•, and the fourth is due to a copolymer radical with an ESR spectrum similar to that of HO–AN•. ESR spectra from pure CAC were interpreted in a previous paper from this laboratory.[6] At an AN monomer concentration of 0.11 mol/L Fischer[10] obtained only monomer radicals. Our data for AN monomer radicals are in good agreement with Fischer's. The residual part of the spectrum is assigned to copolymer radicals M$_1$–AN•, where M$_1$ is CAC. The different radical structures and their designations are collected in Table I. The coupling constants for M$_1$–AN• are given in Table II for comparison with those of HO–AN•.

The Monomer System CNI/AN. In the ESR spectrum for the copolymerizing system CNI/AN (Figure 2), four different components can be observed. They are assigned to the following radicals: CNI–A•, CNI–B•, HO–AN•, and M$_1$–AN•. Coupling constants for M$_1$–AN• radicals are given in Table II.

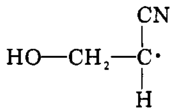
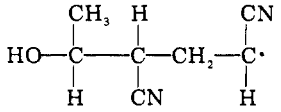
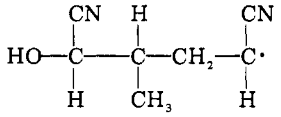
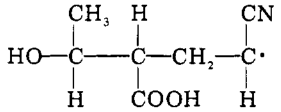
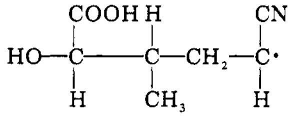
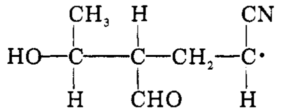
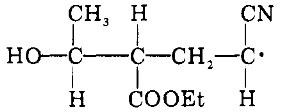
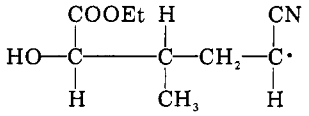
The Monomer System CAD/AN. Figure 3 shows the ESR spectrum from the copolymerizing system CAD/AN. For this system component spectra from the following three radicals could be resolved: CAD–B•, HO–AN•, and M$_1$–AN•. This is in agreement with previous findings[6] that crotonaldehyde only gives HO-CH(CH$_3$)ĊH(CHO) type radicals (monomer tail addition) when attacked by hydroxyl radicals. Coupling constants for M$_1$–AN• are given in Table II.

The Monomer System CAEt/AN. Figure 4 shows the ESR spectrum obtained for the copolymerizing system CAEt/AN. The spectrum for pure CAEt has been interpreted and will be discussed in another study.[12] Four component spectra can be resolved and assigned to: CAEt–A•, CAEt–B•, HO–AN•, and M$_1$–AN•. Coupling constants for M$_1$–AN• are given in Table II.

Discussion

Steric Conformation of Observed Radicals. For aliphatic radicals of the type RH_2C_β–$\dot{C}_\alpha X_1X_2$, the $a_H{}^\beta$ values depend on the average conformation of the radical as given by Heller and McConnell.[13] The relation is $a_H{}^\beta = \rho B_H{}^\beta \cos^2 \theta$, where ρ is the spin density in the $2p_z$ orbital of C_α and θ is the angle between the orbital of the unpaired electron and the C_β–H bonds projected on a plane at right angles to the C_α–C_β bond. If the two protons are equivalent, $a_H{}^\beta$ can be calculated from:[10] $a_H{}^\beta = \rho B_H{}^\beta {}^1\!/\!_4(3 - 2 \cos^2 \varphi)$, where φ is the average angle between the C_β–R bond and the $2p_z$ orbital of the α-carbon atom (Figure 10). $B_H{}^\beta$ is taken as 58.6 G as given by

Table II
Coupling Constants for M_1-AN • Copolymer Radicals

M_1	M_1-AN•	$a_H{}^\alpha$, G	$a_H{}^\beta$, G	$a_H{}^\gamma$, G	$a_N{}^{CN}$, G	Angle φ, deg
HO	 $\mathrm{HO{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$	20.2	28.2		3.6	58.4
CNI	 $\mathrm{HO{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{CN}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$  $\mathrm{HO{-}\overset{CN}{\underset{H}{C}}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$	20.2	21.6	0.8	3.6	41.5
CAC	 $\mathrm{HO{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{COOH}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$  $\mathrm{HO{-}\overset{COOH}{\underset{H}{C}}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$	20.2	21.5	1.2	3.5	41.3
CAD	 $\mathrm{HO{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{CHO}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$	20.2	21.0	1.0	3.5	40.0
CAEt	 $\mathrm{HO{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{H}{\underset{COOEt}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$  $\mathrm{HO{-}\overset{COOEt}{\underset{H}{C}}{-}\overset{H}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CN}{\underset{H}{C}}\cdot}$	20.2	21.5	0.9	3.5	41.3

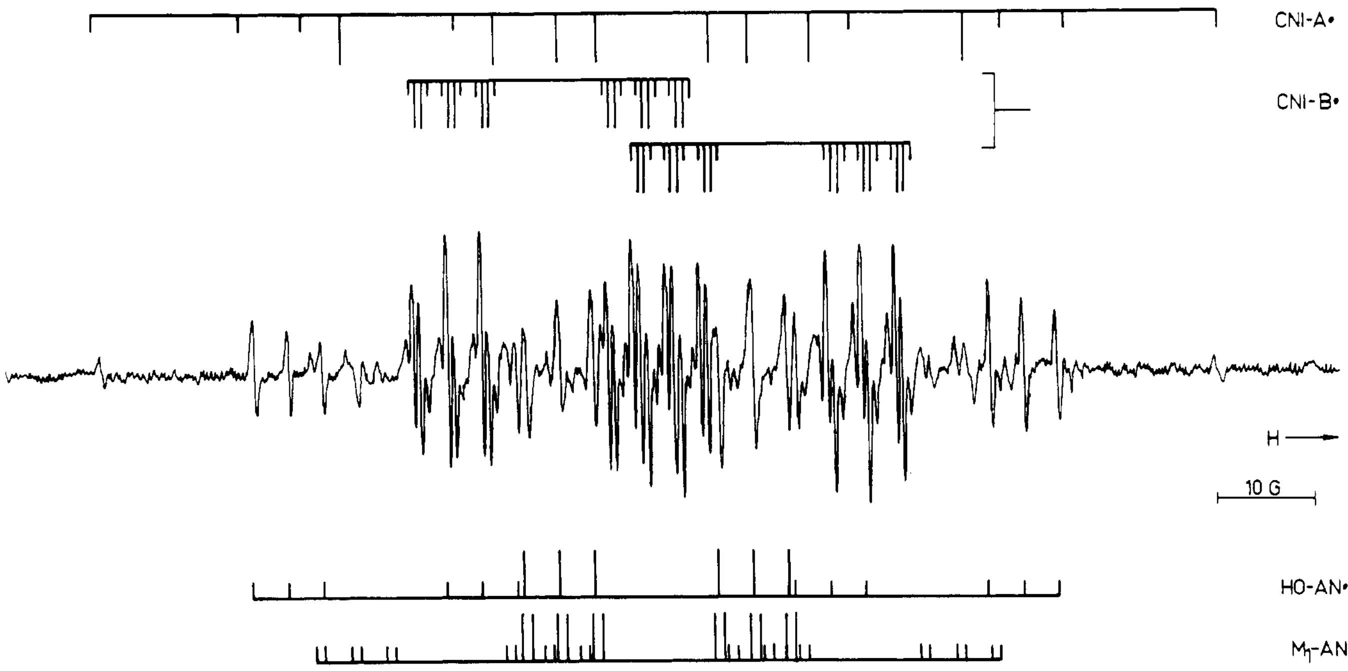


Figure 2. ESR spectrum from the copolymerizing system crotonitrile (CNI)/acrylonitrile (AN) initiated with the redox system H_2O_2-Ti^{3+}: [CNI] = 0.055 mol/L, [AN] = 0.020 mol/L.

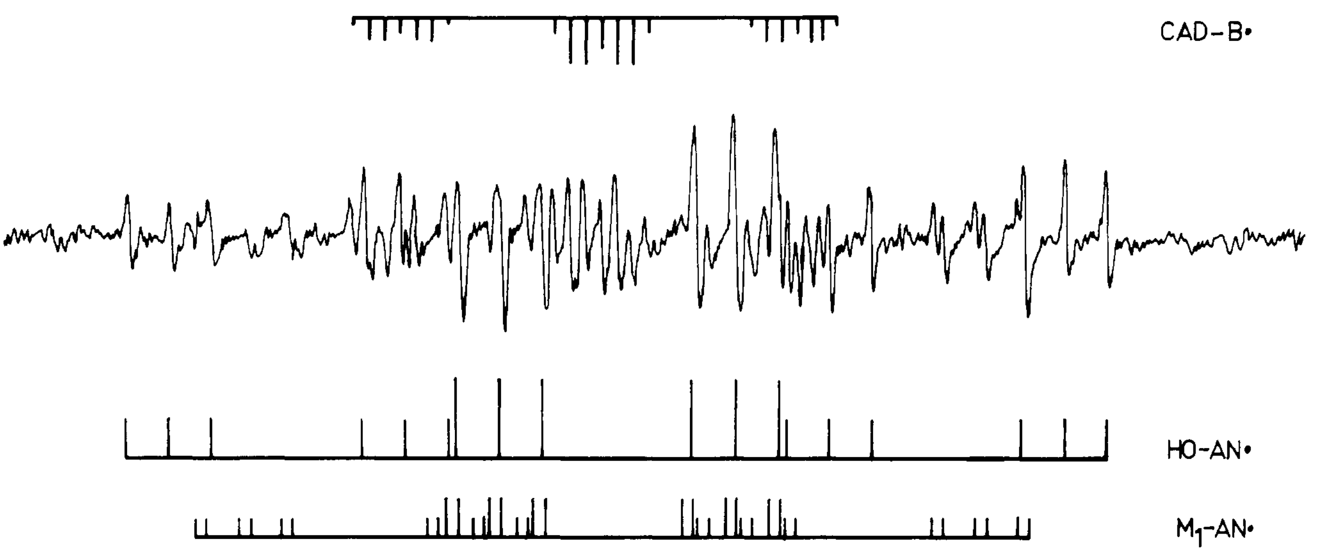


Figure 3. ESR spectrum from the copolymerizing system crotonaldehyde (CAD)/acrylonitrile (AN) initiated with the redox system H_2O_2–Ti^{3+}: [CAD] = 0.055 mol/L, [AN] = 0.020 mol/L.

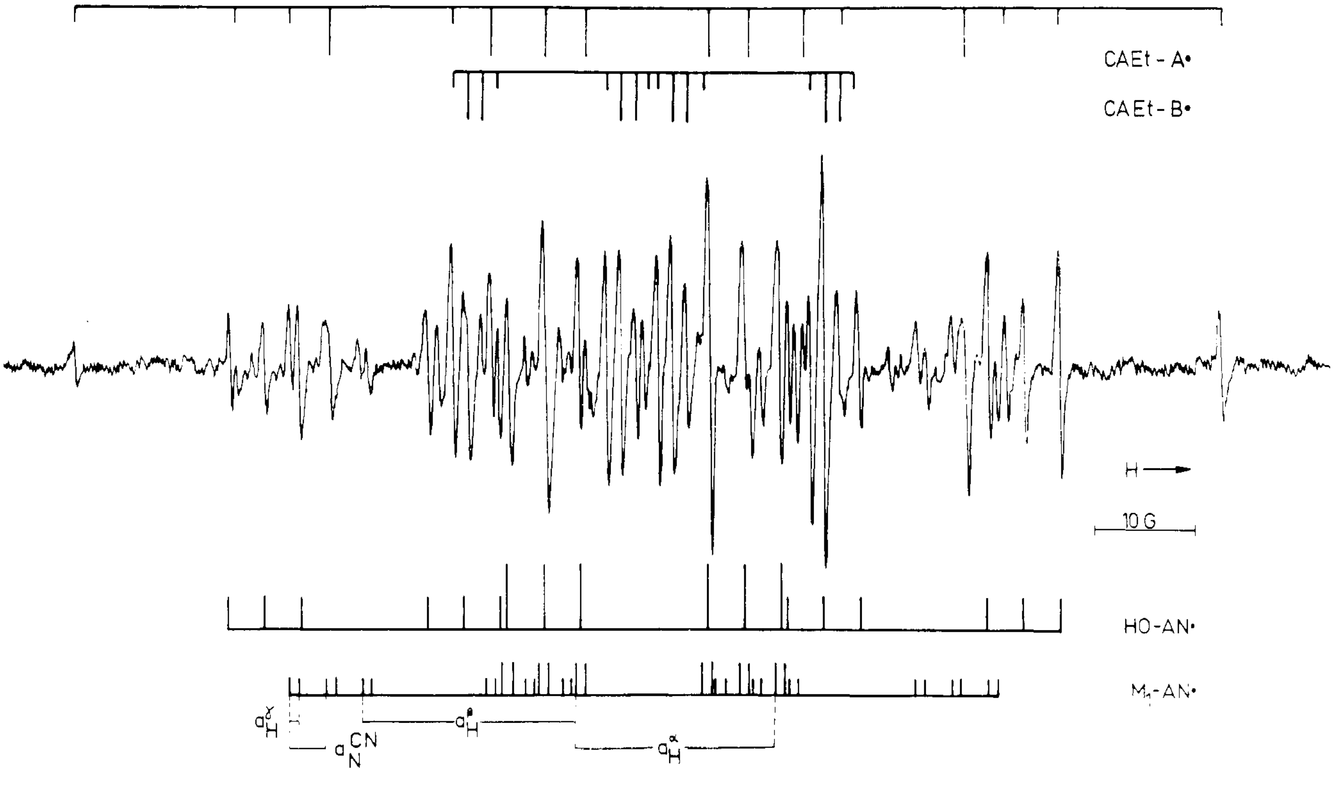


Figure 4. ESR spectrum from the copolymerizing system ethylcrotonate (CAEt)/acrylonitrile (AN) initiated with the redox system H_2O_2–Ti^{3+}: [CAEt] = 0.055 mol/L, [AN] = 0.020 mol/L.

Fessenden and Schuler.[18] The ρ value for the copolymer radical, HO–M_1–AN·, is assumed to be the same as for the AN monomer radical. The value used is 0.785.[10] From these data and the a_H^β values shown in Table II, the φ values shown in Table II are calculated. As expected the exchange of the HO groups in the AN-monomer radicals to the much bulkier HO–M_1 group in the copolymer radicals causes a decrease in the φ values.

The Ratio of A to B Radicals from Crotonic Compounds Formed by HO· Addition. In Table III the concentration ratios of A to B radicals formed by HO· addition to crotonic compounds are collected. The ratio A/B decreases in the following order: CAEt ≈ CAC > CNI > CHO. This is in agreement with the ability of the substituents to stabilize free radicals, Ph > CO ≈ CN > COOR ≈ COOH > CH_3 > H.[14,15] More recent results based on ESR measurements[16] show that a methyl group is more efficient in delocalizing an unpaired electron than a carboxyl group. This would not influence the measured order of decrease in the A/B ratio, but it explains why A/B > 1 for CAC and CAEt.

Relative Reactivity of Crotonic A and B Radicals toward Acrylonitrile. Figures 5–8 show the changes in relative radical concentration as the AN monomer concentration is increased. From the figures the higher reactivity of type A radicals toward AN as compared to type B radicals can be seen for CAC, CNI, and CAEt. From CAD, only B radicals were

Table III
Ratio A/B for Radicals Formed From Crotonic Compounds when Attacked by Hydroxyl Radicals

Monomer	A/B	Monomer	A/B
CAD	0	CAC	2.3
CNI	0.6	CAEt	2.4

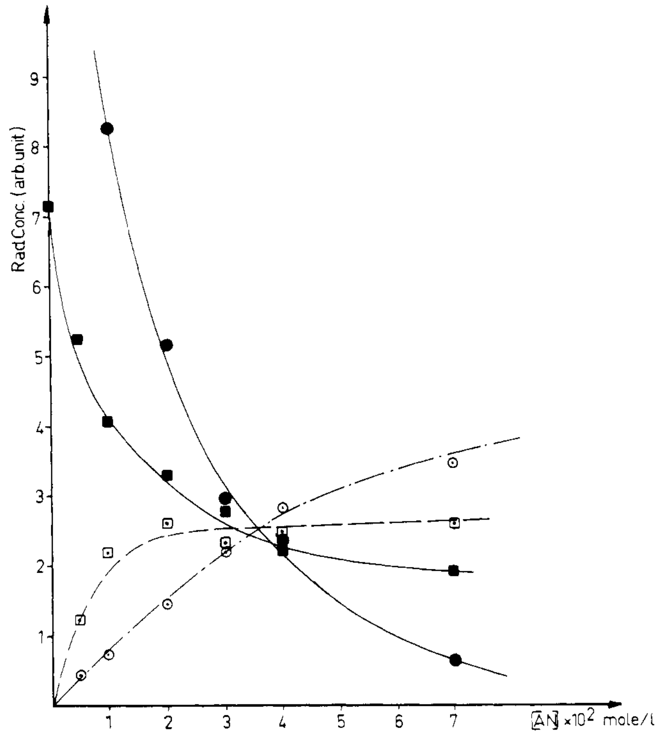


Figure 5. Concentration of different radicals measured from ESR spectra during copolymerization of AN with CAC; [CAC] = 0.055 mol/L; [AN] varies: (●) HO–CH(COOH)$\dot{C}H(CH_3)$ (A radical); (■) HO–$CH(CH_3)\dot{C}H$(COOH) (B radical); (⊙) HO–AN·; (⊡) R–AN· (copolymer radical).

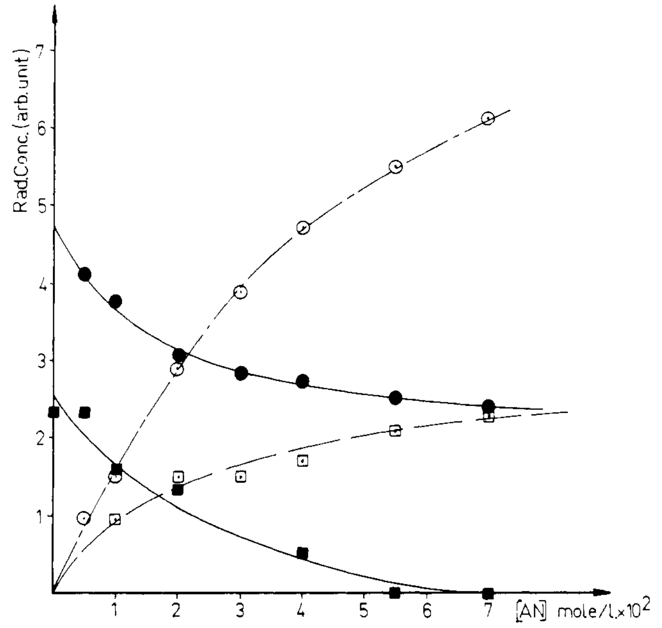


Figure 6. Concentration of different radicals measured from ESR spectra during copolymerization of AN with CNI; [CNI] = 0.055 mol/L; [AN] varies: (●) HO–$CH(CH_3)\dot{C}H$(CN) (B radical); (■) HO–CH(CN)$\dot{C}H(CH_3)$ (A radical); (⊙) HO–An·; (⊡) R–AN· (copolymer radical).

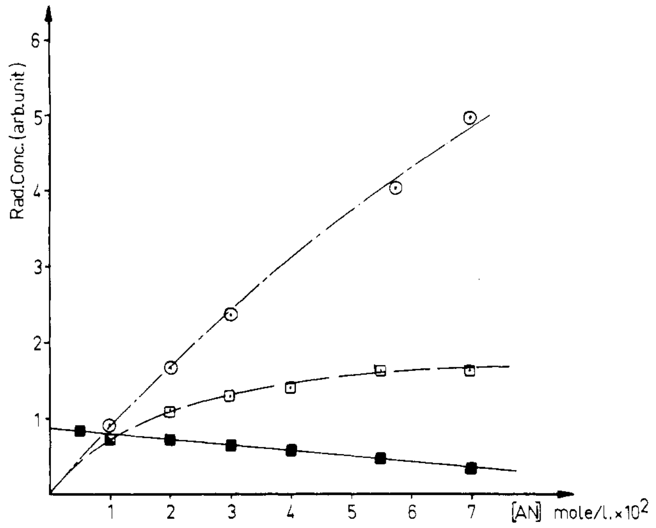


Figure 7. Concentration of different radicals measured from ESR spectra during copolymerization of AN with CAD; [CAD] = 0.055 mol/L; [AN] varies: (■) HO–$CH(CH_3)\dot{C}H$(CHO) (B radical); (⊙) HO–AN·; (⊡) R–AN· (copolymer radical).

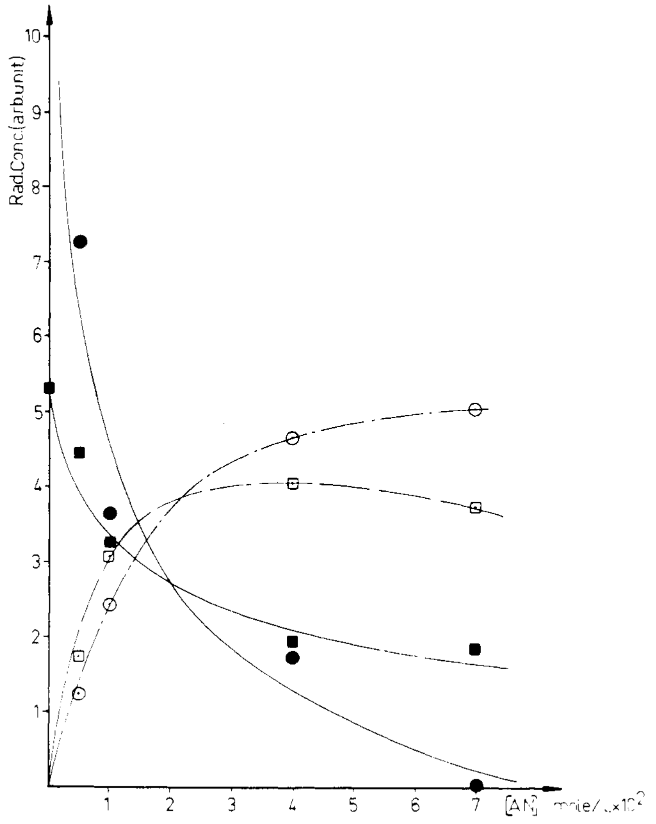


Figure 8. Concentration of different radicals measured from ESR spectra during copolymerization of AN with CAEt; [CAEt] = 0.055 mol/L; [AN] varies: (●) HO–CH(COOEt)$\dot{C}H(CH_3)$ (A radical); (■) HO–$CH(CH_3)\dot{C}H$(COOEt) (B radical); (⊙) HO–AN·; (⊡) R–AN· (copolymer radical).

formed. Also no signal attributable to radicals of the type AN–M_1· could be seen for any monomer. In acrylonitrile, the strongly electron-withdrawing nitrile group gives the double bond a pronounced electrophilic character. In the radicals formed from the crotonic compounds the methyl group is electron donating while all other substituents are electron withdrawing. This polarizes the C_α–C_β bond and makes the carbon atom with the methyl substituent nucleophilic. This should show up as a higher reactivity for type A radicals

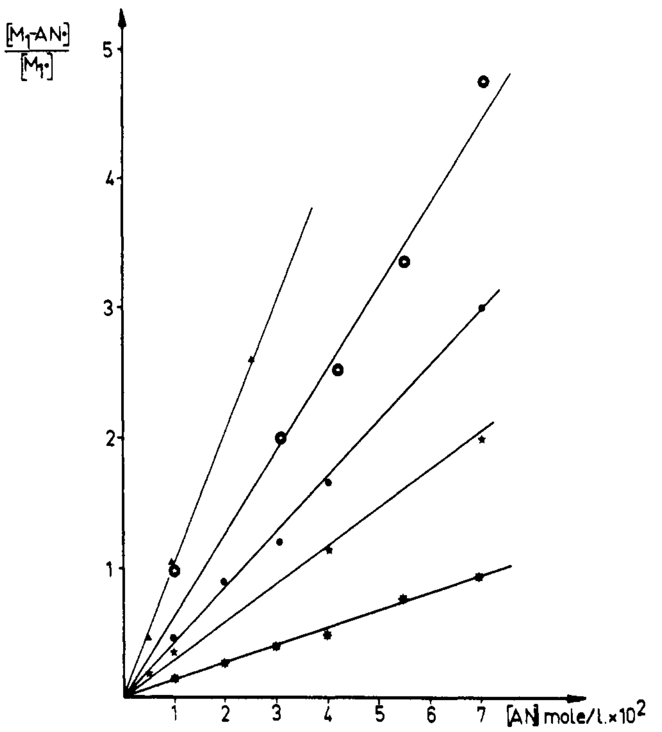


Figure 9. Plots of the concentration ratios $[M_1$-$AN\cdot]/[M_1\cdot]$ vs. [AN] for the systems: (✱) CNI/AN; (▲) VAc/AN; (●) CAC/AN; (★) CAEt/AN; (⊙) CAD/AN. $[M_1] = 0.055$ mol/L, [AN] varies.

toward acrylonitrile, in agreement with our experimental observations.

Effect of Varied Flow Rate. For the system CAC/AN with [CAC] = 0.055 mol/L and [AN] = 0.020 mol/L the effect of changing flow rate was investigated. The flow rate was varied from 3.0 to 7.5 mL/s. In this range the flow cell design used gives complete mixing. Figure 11 shows the ratios $[A\cdot]/[B\cdot]$ and $[CAC$-$AN\cdot]/([A\cdot] + [B\cdot])$ vs. flow rate. For longer reaction times (i.e., low flow rates) it can be seen that A· and B· react to a higher extent with AN to form CAC–AN·. Also the higher reactivity of A· compared to B· can be seen at the lower flow rates, i.e., longer reaction times. These findings support the results from the experiments with changing AN concentration.

Relative Reactivities of Different Monomer Radicals toward Acrylonitrile. The concentration of the copolymer radical M_1–AN· depends on the rate of the reaction

$$M_1\cdot + AN \xrightarrow{v_{12}} M_1\text{–}AN\cdot$$

v_{12} is given by

$$v_{12} = k_{12}[M_1\cdot][AN]$$

Under our reaction conditions in a flow system with a stationary nonequilibrium radical concentration, the M_1–AN· radical concentration is proportional to v_{12}. This implies that the slope (k_{12}') of the straight line in a plot of $[M_1$-$AN\cdot]/[M_1\cdot]$ vs. [AN] is proportional to k_{12} (ref 22). In Figure 9, $[M_1$-$AN\cdot]/[M_1\cdot]$ vs. [AN] is plotted for CAC, CAD, CNI, and CAEt. $[M_1\cdot]$ has been taken as the sum of the two types of free radicals from M_1, i.e., $[M_1$-$A\cdot]$ and $[M_1$-$B\cdot]$. As a reference the same data for vinyl acetate (VAc) as M_1 have been plotted for identical reaction conditions. The measured slopes, k_{12}', are given in Table IV. From the ESR data obtained with the flow system the reactivity of the VAc radicals is 1.5 to 8 times higher than those of the crotonic radicals. In Table IV the literature values[19] of Q and e for CAC, CAD, CNI, VAc, and An are also collected. The calculated $1/r_1$ values according to

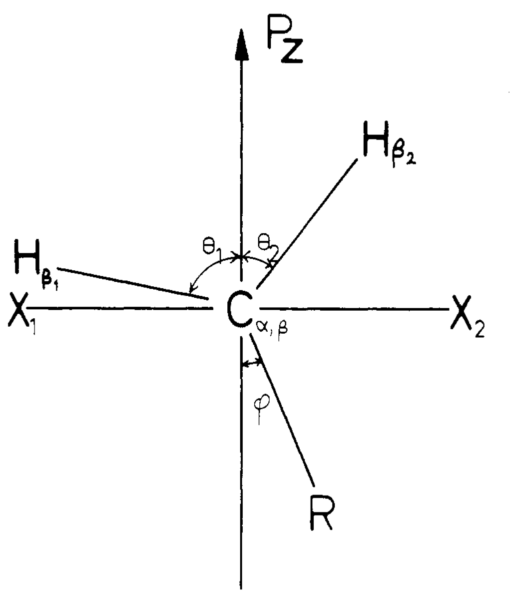


Figure 10. Steric conformation of free radicals of the type R-CH_2-$\dot{C}X_1X_2$ with the C_α-C_β bond at right angles to the paper plane.

$r_1 = Q_1/Q_2 \exp(-e_1(e_1 - e_2))$ are also given in Table IV (column five). These values indicate reactivities of the same magnitude for VAc and the crotonic compounds. However, in the relation

$$k_{12} = P_1 \cdot Q_2 \exp(-e_1e_2) \qquad (1)^{24}$$

from which the expressions for the r values are derived, P_1 is related to the reactivity of the monomer radical M_1, Q_2 is related to reactivity of the monomer M_2, and e_1 and e_2 are polar factors. Since the radical reactivity factors P_1 and P_2 are canceled in the derivation of r_1 and r_2, the r values determined by copolymerization experiments cannot give information about P values. Thus the r values are related to the reactivities of the monomers and not to the reactivities of the monomer radicals. But with the relative k_{12} values determined with ESR it is possible to obtain relative values of P from eq 1. In Table IV, column six gives k_{12}'/Q_2 which is a measure of monomer radical reactivity toward comonomer AN. In eq 1 the term $\exp(-e_1e_2)$ accounts for the polar interactions between radical 1 and monomer 2. The e values are inversely proportional to the dielectric constant of the solvent, so with water as the solvent the term $(-e_1e_2)$ must be divided by 81 (ref 23) which for all practical purposes puts $\exp(-e_1e_2)$ equal to 1. Recalculation of $1/r_1$ values taking the high dielectric constant of water into account gives the $1/r_1'$ values listed in Table IV, column seven.

In radical polymerization it is generally agreed that monomers with limited ability to delocalize unpaired electrons (low Q values) give radicals of high reactivity and vice versa. This can be seen in our results where VAC· is more reactive than all M· formed from the crotonic compounds. Among these CAD· is the most reactive and CNI· the least reactive radical. The reported Q values for crotonic compounds are of the same order of magnitude as the Q value for vinyl acetate. This is remarkable since the $OCOCH_3$ group in vinyl acetate is unable to resonance stabilize an unpaired electron, while the studied crotonic compounds all have substituents with this ability.

Using the Q,e scheme for calculating $1/r_1$ ($=k_{12}/k_{11}$), i.e., the reactivity ratio of monomer radical 1 toward monomer 2 and monomer 1, we obtain the following order of reactivity

$$CAD > CAC > CNI$$

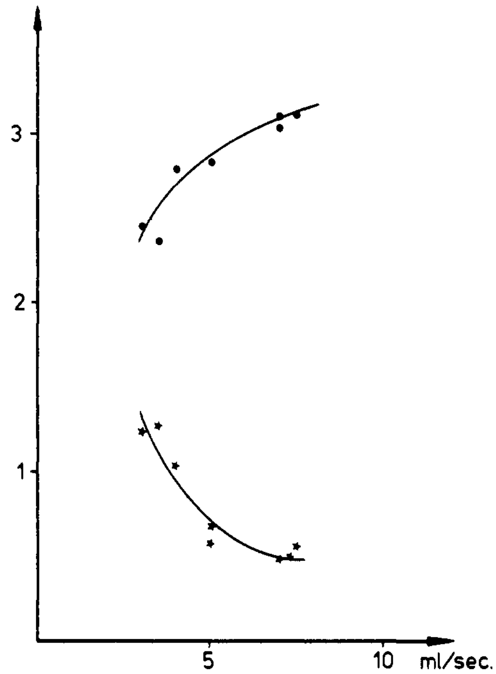


Figure 11. Effect of changing the flow rate on the ratios [A·]/[B·] (●) and [R–AN·]/([A·] + [B·]), (★), [CAC] = 0.055 mol/L and [AN] = 0.020 mol/L.

which agrees nicely with our experimentally found order.

$$\text{CAD} > \text{CAC} > \text{CAEt} > \text{CNI}$$

However, the *Q,e* values used were obtained in solvents with lower dielectric constants than water. Taking this into account by recalculation gives

$$\text{CAD} \approx \text{CAC} > \text{CNI}$$

which still agrees well with out experimental results. Comparing the calculated $1/r_1$ values of the crotonic compounds with $1/r_1$ for vinyl acetate, we find that vinyl acetate radicals should have about the same reactivity toward acrylonitrile as the crotonic radicals. Experimentally we obtain for the radicals:

$$\text{VAc} > \text{CAD} > \text{CAC} > \text{CAEt} > \text{CNI}$$

The copolymerization of vinyl acetate with acrylonitrile is well studied and (r_1, r_2) values are given in the literature, i.e., ref 25. For the crotonic compounds, *Q,e* data are more scarce, making the calculated $1/r_1$ values less reliable. Thus the discrepancy between the measured reactivities and the calculated $1/r_1$ values for the copolymerization of vinyl acetate and the crotonic compounds with the comonomer acrylonitrile can be attributed to the crotonic compounds as a group having very low *Q* values.

Table IV
The Slopes, k_{12}', of the Linear Plots of the Concentration Ratios $[M_1\text{–}AN\cdot]/[M_1\cdot]$ vs. [AN], the Reciprocal Monomer Reactivity Ratio $1/r_1$ Calculated from Literature Values of Q and e,[19] k_{12}'/Q_2, and $1/r_1'$ (See Text)[a]

Comonomer system	k_{12}'	Q_1	e_1	$1/r_1$	k_{12}'/Q_2	$1/r_1'$
VAc/AN	103	0.026	−0.22	31.6	172	23.1
CAC/AN	43	0.013	0.45	32.9	72	46.2
CNI/AN	13	0.016	0.54	26.3	22	37.5
CAD/AN	68	0.013	0.36	34.1	113	46.2
CAEt/AN	30				50	

[a] $Q_2 = 0.60$, $e_2 = 1.20$ (M_2 = AN).

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