Cyclopolymerization: XVIII. Electron spin resonance studies on *N*-methyl-*N*-allylmethacrylamide and allyl crotonate

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E.s.r. studies on *N*-methyl-*N*-allylmethacrylamide (MAMA) and allyl crotonate (AC) were undertaken in order to obtain information on the mechanism of their cyclopolymerization and reactivities of the double bonds involved in these dienes. Amino, hydroxyl and phenyl radicals were used as initiating species. The radicals detected revealed that the rate of intramolecular cyclization of MAMA is faster than that of AC and the methacryloyl group of MAMA has even lower reactivity than allyl and crotonyl groups. The extremely low reactivity of the former is considered to be mainly due to steric hindrance and partly due to the unconjugative nature of its C═C and C═O double bonds.

(Keywords: polymerization; cyclopolymerization; allyl group; e.s.r.)

INTRODUCTION

The cyclopolymerization tendency of unsymmetrical unconjugated dienes with an allyl group varies widely depending on the reactivity of the other double bond. If the latter has higher polymerizability, polymers with extremely low degrees of cyclization are formed and the pendant double bond consists almost exclusively of allyl groups. Some of the typical monomers which belong to this group are *N*-allylacrylamide derivatives[1,2] and allyl esters of methacrylic and acrylic acids[3]. In the case where a double bond other than the allyl group has a lower polymerization tendency, cyclopolymerizability of these dienes is enhanced, as can be seen in the polymerization of *N*-methyl-*N*-allylmethacrylamide (MAMA)[4] and allyl crotonate (AC)[5]. These results are considered to be evidence which substantiates the hypothesis that the lower the polymerizability of the monofunctional counterparts of unconjugated dienes, the higher their cyclopolymerizability, if they polymerize at all[6]. However, the detail of the polymerization mechanisms of these dienes seems to change from monomer to monomer, as is seen in the difference of pendant double bonds detected in the polymers derived from them. Poly(MAMA) contains only the methacryloyl group as pendant unsaturation[4] while poly(AC) has both allyl and crotonyl groups[5]. In order to clarify the polymerization mechanisms of these dienes, e.s.r. studies on them and their monofunctional counterparts have been undertaken.

$R_1-\underset{O}{\underset{\|}{C}}-\underset{CH_3}{\underset{|}{N}}-R_2$	R_1-	R_2-
MAMA	$CH_2{=}\overset{CH_3}{\overset{|}{C}}-$	$CH_2{=}CH-CH_2-$
MAIB	$CH_3{=}\overset{CH_3}{\overset{|}{C}H}-$	$CH_2{=}CH-CH_2-$
MPMA	$CH_2{=}\overset{CH_3}{\overset{|}{C}}-$	$CH_3-CH_2-CH_2-$

$R_3-\underset{O}{\underset{\|}{C}}-O-R_4$	R_3-	R_4-
AC	$\overset{CH_3}{\overset{|}{C}H}{=}CH-$	$CH_2{=}CH-CH_2-$
AB	$CH_3-CH_2-CH_2-$	$CH_2{=}CH-CH_2-$
PC	$\overset{CH_3}{\overset{|}{C}H}{=}CH-$	$CH_3{=}CH_2-CH_2-$

The elemental reactions related to cyclopolymerization of symmetrical 1,6-dienes are illustrated schematically in reactions (1)–(5) in *Scheme 1*. The propagating radicals which possibly appear during the polymerizations are two cyclized radicals and an uncyclized radical. Either radical or a mixture of them would be detected on e.s.r. measurements depending on the rate-determining step of cyclopolymerization and the cyclic structure formed. In the case of unsymmetrical unconjugated dienes, the situation is rather complicated, because the number of radicals detected would be twice as high. However, if interpretation of the results obtained is possible, the information on the reactivity of the two double bonds involved could be available in addition to that of the rate-determining step. In connection with these considerations, determination of the reactivities of the methacryloyl and crotonyl groups with respect to those of allyl groups is interesting, since they contain double

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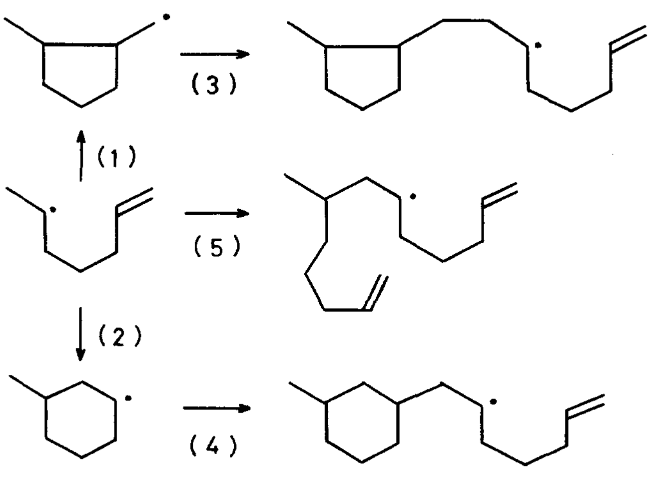


Scheme 1 Reactions related to cyclopolymerization of symmetrical 1,6-dienes

bonds with extremely low reactivity. Amino, hydroxyl and phenyl radicals were adopted as initiating species, since their reactivities differ widely.

EXPERIMENTAL

Materials

Methacrylamide derivatives and allylamine derivatives were synthesized by interfacial condensation reaction between corresponding amines and acid chlorides based on the procedure for the preparation of sym-dimethyldimethacryloylhydrazine[7]. Esters were synthesized by condensation of corresponding alcohols and acids according to the procedure reported[8].

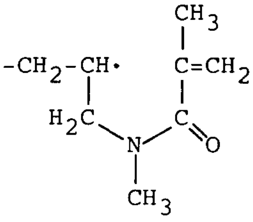
Measurements

The e.s.r. spectra were recorded using a flow system with a TE011 mode cylindrical cavity of a JES-FE1X spectrometer from Jeol Ltd, Tokyo. The flow rate used was 2.5 $cm^3 s^{-1}$. This flow rate corresponds to a time lag before measurement of about 0.03 s. The methods used for the generation of hydroxyl[9], amino[10] and phenyl[11] radicals were similar to those previously described. The pH was adjusted to 1.4 by adding sulphuric acid. The monomer concentration used was usually 0.05 mol dm^{-3} except for the case initiated by the phenyl radical where 0.1 mol dm^{-3} of monomer concentration was adopted. All measurements were made at room temperature (25 ± 2°C). The magnetic field was calibrated with a Mn^{++} sample. In the case of monomers which are sparingly soluble in water, measurements were carried out in water mixed with methanol at 30% by volume. These are AC, allyl butyrate (AB) and propyl crotonate (PC). Computation of isotropic hyperfine splitting constants was carried out based on the program reported[12].

RESULTS

E.s.r. spectra of MAMA initiated by amino radical

MAMA yields polymers with a degree of cyclization higher than 90% even in bulk polymerization. The repeating cyclic unit of poly(MAMA) consists of a five-membered ring and residual unsaturation detected as a minor repeating structure is only the methacryloyl group of the two possible unsaturations[4]. These results indicate that the possible propagating radicals which appear during the polymerization of MAMA are radicals I–IV.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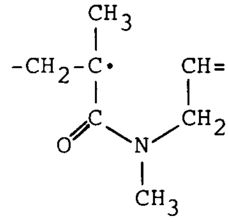
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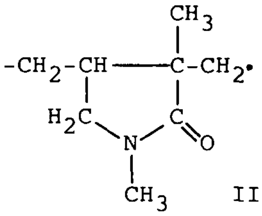
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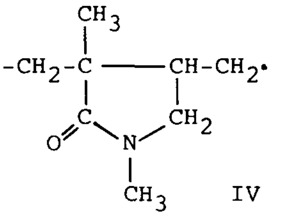

IV

E.s.r. spectra of MAMA measured using the amino radical are illustrated in *Figure 1*. The three-line spectrum with intensities of 1:2:1 is attributed to the cyclized radical III (No 1 in *Table 1*). Signal B (a quartet of triplets of triplets of triplets) can be ascribed to either of two uncyclized radicals, V or VI. The spectral pattern depicted in *Figure 1D* appears for radical V on simulation assuming that two of the four β-methylene protons and the α-proton have a coupling constant of 2.203 mT and the other two β-methylene protons have a splitting constant of 2.370 mT with contributions of the splitting constant of 0.380 mT from $>N-CH_3$ nitrogen and of 0.590 mT from $-NH_2$ nitrogen. In addition, the same

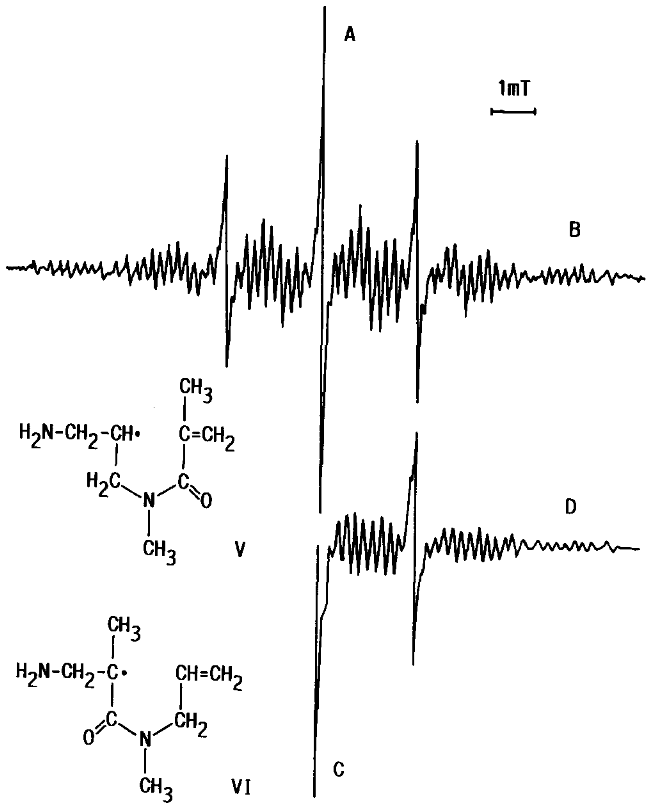
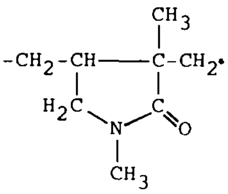
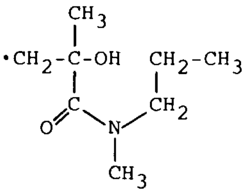


Figure 1 E.s.r. spectra of MAMA initiated by the amino radical. (A) and (B) Observed spectrum; (C) and (D) computed line shape for radicals III and V using splitting constants given in *Tables 1* (No 1) and *2* (No 4) and a Gaussian line width ΔH = 0.08 mT. The proportion of radicals V and III was assumed to be 7:3

pattern as that of *Figure 1D* is derived from radical VI with $a(\beta CH_3) = 2.203$ mT, $a(\beta CH_2) = 2.370$ mT, a(N in N–CH_3) = 0.380 mT and a(N in NH_2) = 0.590 mT. The splitting constants of $>N-CH_3$ and $-NH_2$ nitrogens were determined based on the fact that the coupling constants of amino nitrogens added to allyl groups are around 0.5 mT[10]. This can be also seen in radicals VII and XIX which are shown later.

The assignment of the spectrum B is critical for understanding the fundamental aspects of the cyclopolymerization of MAMA. For this reason, e.s.r. spectra of its monofunctional counterparts, i.e. *N*-methyl-*N*-allylisobutanamide (MAIB) and *N*-methyl-*N*-propylmethacrylamide (MPMA), were measured using the amino radical and are illustrated in *Figures 2* and *3*, respectively. The spectrum derived from MAIB is ascribed to radical VII judging from its good coincidence with the computed line shape using the coupling constants described in *Table 2* (No 1). Comparison of

Table 1 Coupling constants of radicals derived from MAMA and MPMA

Radical detected		I^a	a (αCH_2) (mT)	No
	III	$H_2N^{\bullet}$	2.170	1
		$HO^{\bullet}$	2.190	2
		$C_6H_5^{\bullet}$	2.160	3
	XIV	$HO^{\bullet}$	2.150	4

[a] Initiation radical

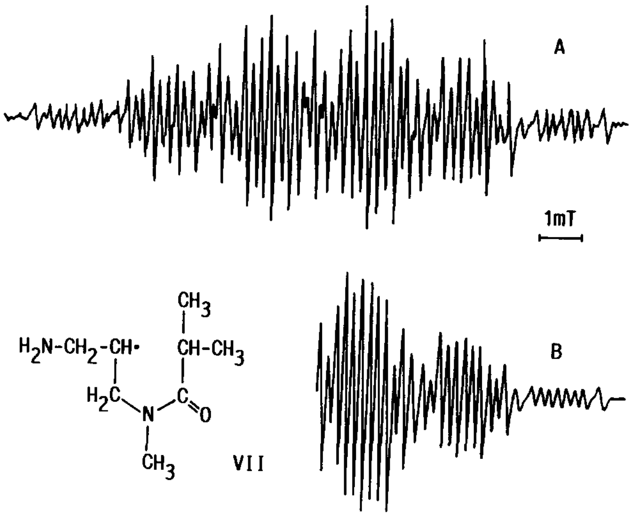


Figure 2 E.s.r. spectrum of MAIB initiated by amino radical. (A) observed spectrum; (B) computed line shape for radical VII using coupling constants given in *Table 2* (No 1) and a Gaussian line width $\Delta H = 0.08$ mT

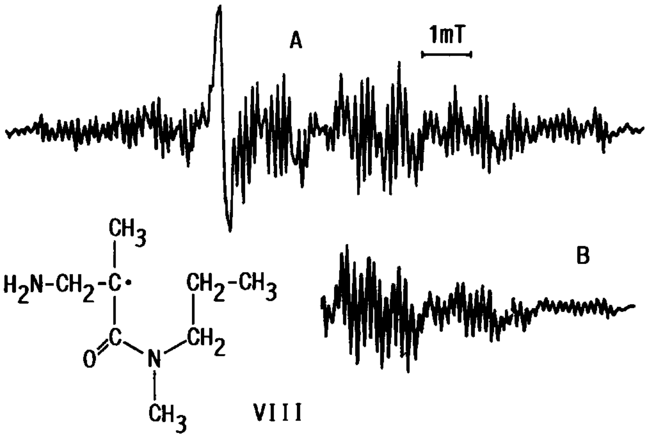
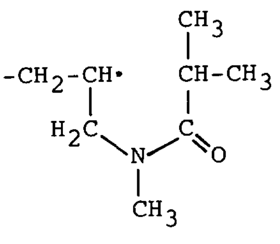
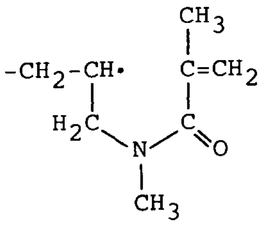


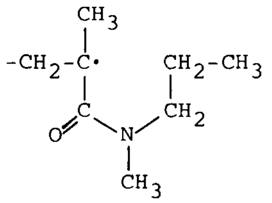
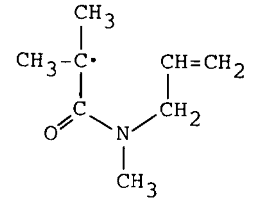
Figure 3 E.s.r. spectrum of MPMA initiated by amino radical. (A) Observed spectrum; (B) computed line shape for radical VIII using coupling constants given in *Table 3* (No 1) and a Gaussian line width $\Delta H = 0.08$ mT

Table 2 Coupling constants of radicals derived from MAMA and MAIB

Radical detected		I^a	a(αCH) (mT)	$a(\beta CH_2)_1$ (mT)	$a(\beta CH_2)_2$ (mT)	$a(N)_{CH_3}$ (mT)	$a(N)_{H_2}$ (mT)	No
	VII	$H_2N^{\bullet}$	2.180	2.180	2.385	0.380	0.585	1
	$X_a{}^b$	$HO^{\bullet}$	2.120	2.120	2.310	0.390	–	2
	$X_b{}^b$	$HO^{\bullet}$	2.100	2.100	2.535	0.350	–	3
	V	$H_2N^{\bullet}$	2.203	2.203	2.370	0.380	0.590	4
	I	$HO^{\bullet}$	2.190	2.190	2.394	0.408	–	5
	I	$C_6H_5^{\bullet}$	2.190	2.190	2.394	0.408	–	6

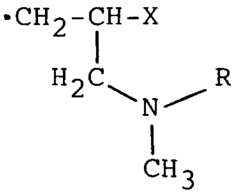
[a] Initiation radical
[b] Conformational isomers of X

Table 3 Coupling constants of radicals derived from MPMA and MAIB

Radical detected		I^a	$a(\beta CH_3)$	$a(\beta CH_2)$	$a(CH_3)_N$	$a(CH_2)_N$	$a(N)_{CH_3}$	$a(N)_{H_2}$	No
			(mT)						
	VIII	$H_2N^\bullet$	2.280	1.675	0.130	0.130	0.130	0.510	1
	XIII	$HO^\bullet$	2.250	1.730	0.130	0.130	0.130	-	2
	XI	$HO^\bullet$	2.170	-	0.110	0.110	0.110	-	3

[a] Initiation radical

Table 4 Coupling constants of radicals derived from MAMA and MAIB

Radical detected		X	R	$a(\alpha CH_2)$	$a(\beta CH)$	No
				(mT)		
	IX	HO-	$CH_2{=}C(CH_3)CO-$	2.241	2.394	1
	XII	HO-	$(CH_3)_2CHCO-$	2.187	2.425	2
	XVII	C_6H_5-	$CH_2{=}C(CH_3)CO-$	2.180	2.370	3

signal B in *Figure 1* and that of MAIB allows us to assign the former to radical V. It can be noticed that almost the same coupling constants have been obtained for both the radical species (see Nos 1 and 4 in *Table 2*). The fact that the spectral pattern obtained from MPMA (*Figure 3A*) is different from that of B in *Figure 1* is additional support for this conclusion. This is because the former can be assigned to radical VIII based on the good agreement between the observed and computed patterns except for a broad peak detected at lower magnetic fields derived from unknown species. Coupling constants determined for radical VIII are given in *Table 3* (No 1).

E.s.r. spectra of MAMA initiated by hydroxyl and phenyl radicals

An e.s.r. study on MAMA by the rapid flow technique using hydroxyl radicals has already been reported[2]. Its spectrum is reproduced in *Figure 4*. The three-line spectrum with an intensity of 1:2:1 has been attributed to the cyclized radical III (No 2 in *Table 1*). It has been shown that the signal B is contaminated with radical IX (No 1 in *Table 4*) but the problem was that it could be ascribed to either of two uncyclized radicals, I or II, as in the case of spectrum B in *Figure 1*. In order to identify radical species which yield signal B in *Figure 4*, e.s.r. spectra of its monofunctional counterparts, i.e. MAIB and MPMA, were measured using the hydroxyl radical as an initiating species.

The results are illustrated in *Figures 5* and *6*. The spectrum derived from MAIB (*Figure 5A*) contains radical X as a main component and radicals XI and XII as minor components. It appears that radical X exists in two conformers, though the reason is not clear at present. Simulation assuming the coupling constants given in *Tables 2* (Nos 2 and 3), *3* (No 3) and *4* (No 2) yielded a spectral pattern which is in good agreement with the observed spectrum. Comparison of the coupling constants of radical I (No 5 in *Table 2*) with those of radicals X_a and X_b (Nos 2 and 3 in *Table 2*) allows us to assign the former to radical I. Radical XIII (No 2 in *Table 3*) derived from the methacryloyl group of MPMA (*Figure 6B*) gives a different spectral pattern from that of B in *Figure 4*. This is another indication that the spectrum B in *Figure 4* cannot be assigned to the uncyclized radical II.

One problem is that the spectrum of MPMA contains a triplet, which is attributable to the head radical XIV (No 4 in *Table 1*), along with the signals of radical XIII and other unknown minor components. Therefore, one may doubt that the triplet in *Figure 4* is due to radical XV and not due to the cyclized radical III. However, it must be noticed that the proportion of radical XIV to radical XIII is small in contrast to the considerably higher content of the radical which yields a triplet in *Figure 4*. In addition, the fact that a triplet with almost the same splitting constant was observed in the MAMA initiated by the amino radical (*Figure 1A*) supports the conclusion that the main radical which produces the triplet in *Figure 4* is radical III. In the case of MAMA initiated by an

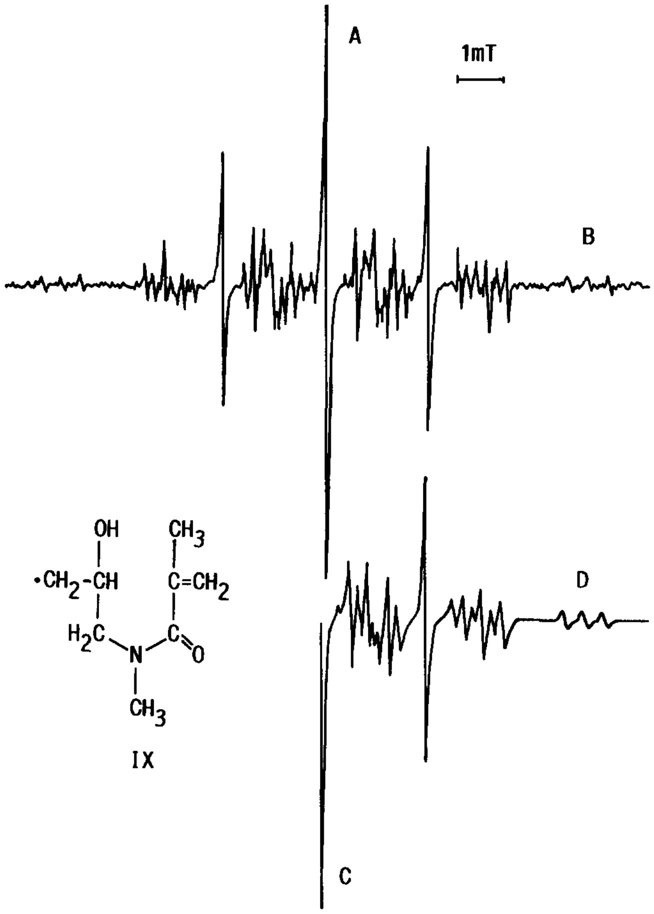
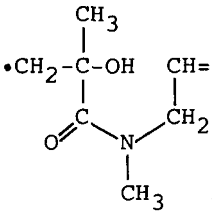
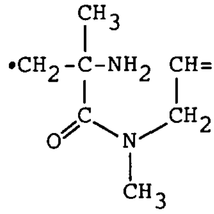


Figure 4 E.s.r. spectrum of MAMA initiated by hydroxyl radical (reproduced from ref. 2 with the permission of the publishers; Hüthig and Wepf Verlag, Basel). (A) and (B) Observed spectrum; (C) and (D) computed line shape for radicals III, I and IX using splitting constants given in *Tables 1* (No 2), *2* (No 5) and *4* (No 1) and a Gaussian line width $\Delta H = 0.08$ mT. The proportion of radicals I, III and IX was assumed to be 0.5:0.4:0.1



XV



XVI

amino radical, the head radical XVI cannot be a triplet because of the splitting by nitrogen of the initiating species added.

Figure 7 indicates the spectrum of MAMA initiated by the phenyl radical. It is essentially the same as that of MAMA initiated by the HO• radical. Computation assuming the coupling constants given in *Tables 1* (No 3), *2* (No 6) and *4* (No 3) for radicals III, I and XVII, respectively, yielded a spectral pattern illustrated in *Figure 7C* and *D* which shows good coincidence with the observed spectrum. In spite of the fact that there is a large difference in the reactivities of the initiating radicals employed, the main radicals observed in MAMA are fundamentally the same, i.e., radicals I and III.

E.s.r. spectra of AC

The spectra shown in *Figure 8A* were obtained from AC initiated by the amino radical. The signal to noise ratio is low in this spectrum but it can be seen that it has a similar pattern to that of radical XIX derived from allyl butyrate (AB) measured using the amino radical (*Figure 8B*), which is in turn in good agreement with the computed spectrum shown in *Figure 8C*. These results reasonably lead to the conclusion that spectrum A is due to radical XVIII. The splitting constants adopted for the simulation are given in *Table 5*. The coupling constant for $-CH_2-N<$ protons was assumed to be

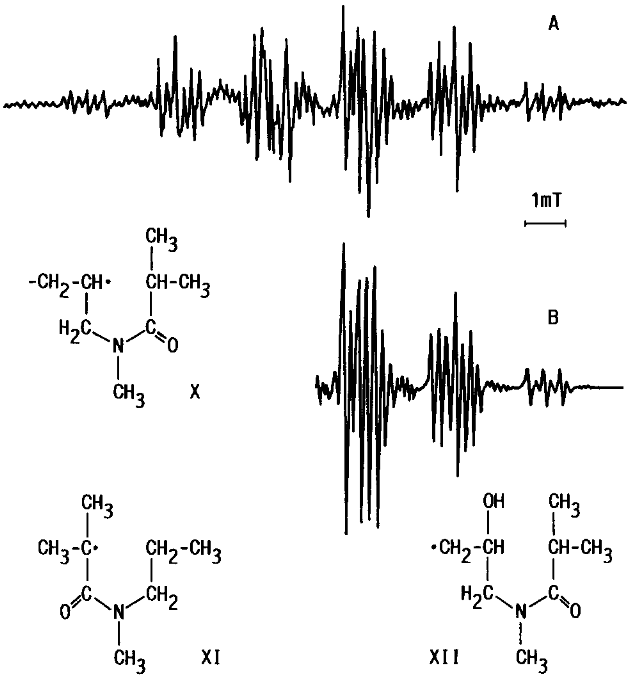


Figure 5 E.s.r. spectrum of MAIB initiated by hydroxyl radical. (A) Observed spectrum; (B) computed line shape for radicals X_a, X_b, XI and XII using splitting constants given in *Tables 2* (Nos 2 and 3), *3* (No 3) and *4* (No 2) and a Gaussian line width $\Delta H = 0.08$ mT. The proportion of the radicals X_a, X_b, XI and XII was assumed to be 0.55:0.23:0.10:0.12. The radicals X_a and X_b are conformational isomers of X

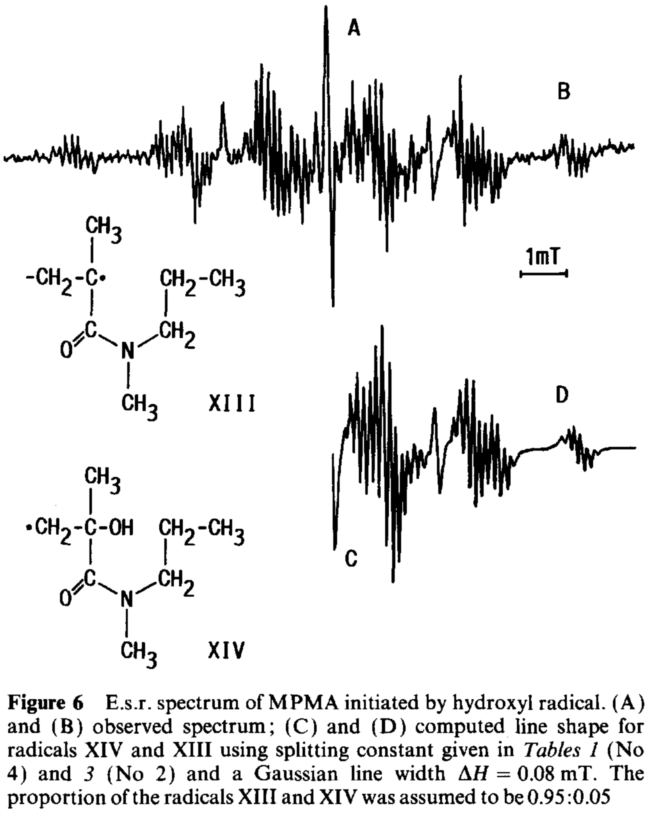


Figure 6 E.s.r. spectrum of MPMA initiated by hydroxyl radical. (A) and (B) observed spectrum; (C) and (D) computed line shape for radicals XIV and XIII using splitting constant given in *Tables 1* (No 4) and *3* (No 2) and a Gaussian line width $\Delta H = 0.08$ mT. The proportion of the radicals XIII and XIV was assumed to be 0.95:0.05

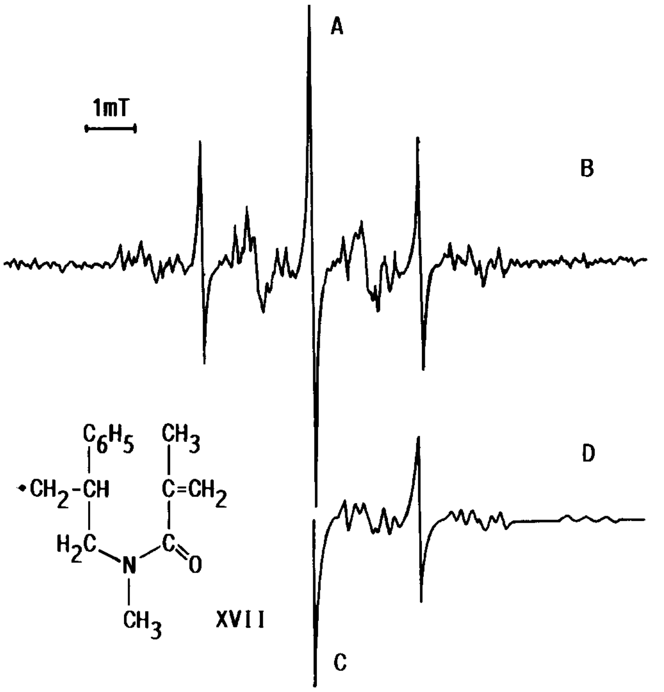


Figure 7 E.s.r. spectrum of MAMA initiated by phenyl radical. (A) and (B) Observed spectrum; (C) and (D) computed line shape for radicals III, I and XVII using splitting constants given in *Tables 1* (No 3), *2* (No 6) and *4* (No 3) and a Gaussian line width $\Delta H = 0.11$ mT. The proportion of radicals I, III and XVII was assumed to be 0.44:0.46:0.10

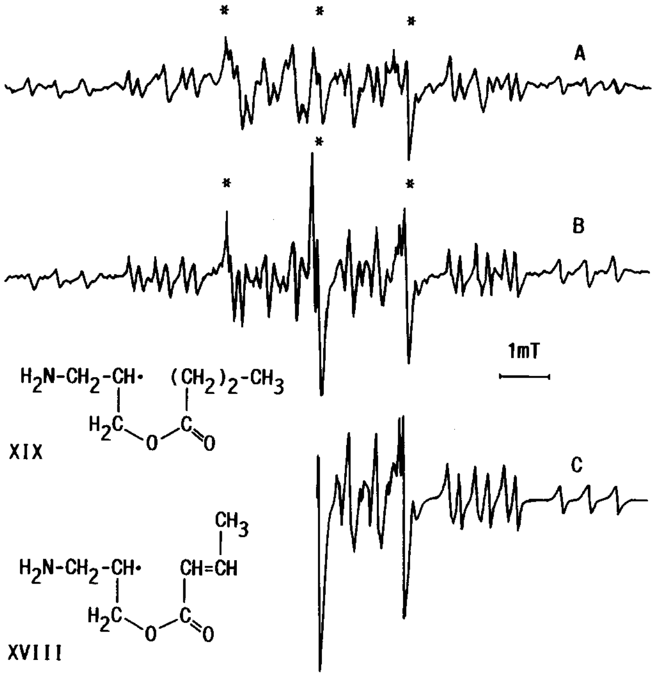


Figure 8 E.s.r. spectra of AC and AB initiated by amino radical. (A) and (B) Observed spectra for AC and AB, respectively. Signals with asterisks are due to radical XX. (C) Computed line shape for radicals XIX and XX using splitting constants given in *Table 5* and a Gaussian line width $\Delta H = 0.065$ mT. The proportion of radicals XIX and XX was assumed to be 0.72:0.28

larger than that of $-CH_2-O-$ protons based on the fact that the coupling constant for $a(\beta CH_2)$ of radical $H_2N-CH_2-\dot{C}H-CH_2-NH_2$ is larger than that for radical $HO-CH_2-\dot{C}H-CH_2-OH$[10]. The six-line signal with the asterisk is due to radical XX derived from methanol.

$$^{\bullet}CH_2OH \qquad XX$$

Figure 9 shows the e.s.r. spectra of AC and propyl crotonate (PC) initiated by the hydroxyl radical. The six-line signal of radical XX is also observed in these spectra. The other complicated signal A is assigned to radical XXI, judging from the good coincidence with that of radical XXII derived from PC, shown in *Figure 9B*. The splitting constants of each proton involved which are shown in *Table 5* were obtained based on the simulation. The good agreement between observed and computed line shapes (*Figure 9C*) can be recognized.

The hydroxyl group has not been depicted in the radicals detected by using the HO$^{\bullet}$ radical except for the species XXI and XXII. This is because evidence for the presence of hydroxyl groups is not available, unlike the case where the amino group is attached. However, results[10] reported so far suggest that these radicals obtained by using hydroxyl radicals are also monomeric. In addition, the fact that the monomer concentration employed for e.s.r. measurements is as low as 0.05 mol dm^{-3} also supports the above consideration. Especially in the case of the radical derived from AC, its structure is considered to be ascribable to XXI based on the following argument.

Table 5 Coupling constants of radicals derived from AC, AB and PC

Radical detected[b]	I[a]	$a(\alpha CH)$	$a(\beta CH_2)_N$	$a(\beta CH_2)_O$	$a(N)$
		(mT)			
XVIII, XIX	$H_2N^{\bullet}$	2.170	2.230	2.000	0.550
Radical detected[b]	I[a]	$a(\alpha CH)$	$a(\beta CH)$	$a(\gamma CH_3)$	$a(\gamma CH_2)_O$
		(mT)			
XXI, XXII	HO$^{\bullet}$	1.990	1.200	0.070	0.140

[a] Initiation radical
[b] Radical XX ($a(CH_2) = 1.730$, $a(OH) = 0.090$ in mT) was also detected

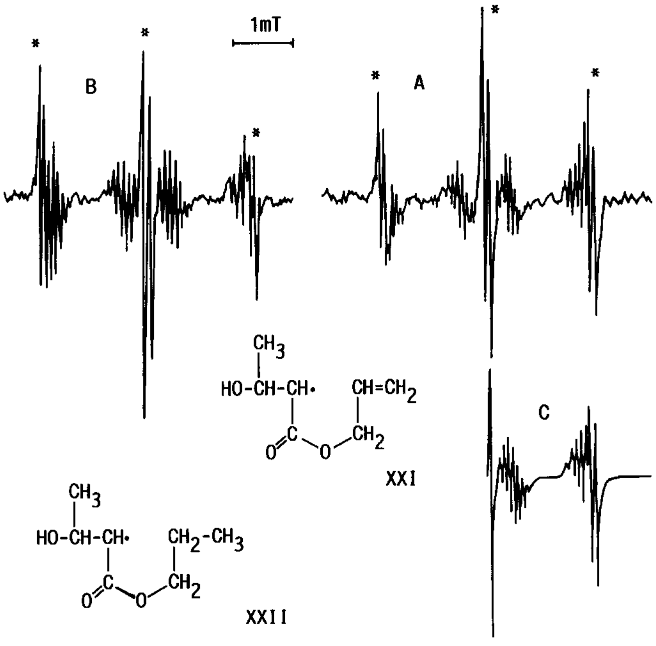


Figure 9 E.s.r. spectra of AC and PC initiated by hydroxyl radical. (A) and (B) Observed spectra for AC and PC, respectively. Signals with asterisks are due to radical XX. (C) Computed line shape for radicals XXI and XX using splitting constants and a Gaussian line width $\Delta H = 0.042$ mT. The proportion of radicals XXI and XX was assumed to be 0.64:0.36

Since poly(AC) contains allyl and crotonyl groups as pendant unsaturation[5], it can be understood that propagating radicals attack both the double bonds of AC during its polymerization. This means that if polymeric propagating radicals could be observed, at least two species should be detected. On the contrary, only one radical was observed in the case where AC was measured using the OH radical as in the case triggered by the amino radical. This indicates that the monomeric radical XXI is observed probably due to the selective reactivity of the hydroxyl radical towards the crotonyl group. For this reason, the hydroxyl group was depicted in radicals XXI and XXII.

The results obtained show that the hydroxyl radical has higher reactivity towards the crotonyl group than towards the allyl group and in addition it attacks preferentially the side of the methyl group of the crotonyl group but not that of the carbonyl group. This can be also seen in the reactivity of PC. The reaction behaviour of crotonyl groups of AC and PC is different from that of crotonic acid. Both carbons of the C=C double bond of crotonic acid are attacked by the hydroxyl radical[13]. On the contrary, it is the allyl group of the two double bonds of AC that is attacked by the amino radical. The difference in reactivities observed in these initiating radicals is consistent with the reported electrophilicities, which decrease in the order, $H_2N^\bullet > HO^\bullet$[14].

DISCUSSION

Comparison of the coupling constants of radicals derived from MAIB, MPMA and MAMA summarized in *Tables 2* and *3* clearly indicates that the spectra in *Figures 1B*, *4B* and *7B* are derived from the allyl group of MAMA. Accordingly, the main radicals observed in MAMA are fundamentally the same, i.e., radicals I and III, irrespective of the fact that there is a large difference in the reactivities of the initiating radicals employed. Even initiation by the phenyl radical which has a nucleophilic character[15] yields radicals I and III. This strongly indicates that the polymerization of MAMA begins exclusively from the side of allyl group. The structural studies reported are in accordance with this conclusion, since they revealed that the pendant double bonds in poly(MAMA) consist of only the methacryloyl group[4]. These results reasonably lead to the conclusion that the reactivity of the methacryloyl group of MAMA is even lower than that of the allyl group. E.s.r. studies of AC suggest that polymerization of AC begins from either side of the double bonds, depending on the reactivity of the attacking radical, in agreement with the fact that both the double bonds of AC are observed in poly(AC)[5]. Based on these results, it is reasonable to conclude that the methacryloyl group of MAMA is less reactive than the crotonyl group of AC.

N.m.r. studies showed that the C=C and C=O double bonds of the *N,N*-disubstituted methacrylamide group have an unconjugative nature in contrast to their appearance, owing to the twisted conformation between the carbonyl group and the olefin double bond[16]. This would be one reason for the lower reactivity of the *N,N*-disubstituted methacrylamide group toward radicals. However, it must be noticed that it is less reactive than the allyl group which is one of the typical unconjugated double bonds. Furthermore, it was found that the *N,N*-disubstituted methacrylamide group has lower reactivity than the crotonyl group whose reactivity is low because of steric hindrance. Based on these results, it is suggested that the main factor which governs the extremely low polymerizability of the *N,N*-disubstituted methacrylamide group is due to steric hindrance, and the contribution from its unconjugative nature derived from the twisted conformation of its C=C and C=O double bonds should also be taken into account, though the latter is less important than the steric factor.

The experimental conditions for the rapid-flow technique are different from those adopted in ordinary radical polymerization. Discussion on the rate-determining step of the cyclopolymerization of unconjugated dienes should be based on e.s.r. studies on the polymerization system in the stationary state. Nevertheless, significant aspects of the polymerization can be brought to light by comparing the various experimental results.

It has been reported that only cyclized radicals are detected when e.s.r. studies on several diallyl compounds using amino, hydroxyl and phenyl radicals generated in a flow system are carried out[17,18]. The present investigation on MAMA shows that the MAMA is attacked exclusively from the side of the allyl group and the main radicals detected are I and III. In the case of AC, polymerization begins from both the double bonds and only the uncyclized radical is observed irrespective of the double bonds involved in polymerization. Based on these results, it can be said that the rates of intramolecular cyclization are considered to decrease in the order of diallyl compounds, MAMA and AC. In accordance with these results, the degree of cyclization of their polymers obtained decreases in the same order, i.e., diallyl compounds[19], MAMA[4] and AC[5,20].

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