

ALTERNATING COPOLYMERIZATION OF VINYL COMPOUNDS IN THE PRESENCE OF ORGANOMETAL HALIDES

Masaaki Hirooka

Sumitomo Chemical Co. Ltd., 2-7-9, Nihonbashi, Chuo-ku, Tokyo, Japan

Abstract - Alternating copolymerization of vinyl compounds complexed with (organo)metal halides is reviewed and discussed in terms of the mechanisms. The reaction proceeds through radical species to give an alternating copolymer. The organo-metal halide plays an important role in the propagation as well as initiation steps and causes abnormal kinetic relations, inert nature towards the degradative chain transfer of allyl resonance monomers and less chain transfer reactions towards conventional transfer reagents.

Charge transfer interactions of the metal halide and monomers at the growing chain end seem to be important and a mechanism involving such charge transfer interaction is likely to explain the alternating regulation and the anomalous phenomena.

INTRODUCTION

In conventional radical processes, alternating copolymers of vinyl compounds have been obtained only in combinations of specific acceptor monomers with donor monomers. In 1963, a new concept to control the sequential structure of copolymers was introduced in which metal halogenides regulate the monomer reactivities to lead to alternating copolymers by complex formation (Refs. 1 to 4).

Before that, Bamford et. al. (Ref. 5) first found a promoting effect of lithium chloride on the polymerization of acrylonitrile and then similar accelerating effects of other metal halides such as zinc chloride (Refs. 6-8) and aluminum halide (Ref. 9) were revealed. Alkylaluminum halides (Refs. 1-4) were found to be specifically effective in giving alternating copolymers of conjugated vinyl monomers having a nitrile or carbonyl group (B group) and donor monomers (A group).

RADICAL CHARACTER OF COPOLYMERIZATION

Alternating copolymerization with an alkylaluminum halide proceeds spontaneously and is promoted by organic peroxides and oxygen. The rate of copolymerization of styrene and methyl acrylate with ethylaluminum sesquichloride is proportional to the square root of benzoyl peroxide concentration as shown in Fig. 1 (Ref. 10). The rate of polymerization is considerably accelerated also by u.v. irradiation and is proportional to the square root of the light intensity (Ref. 11). These phenomena suggest that the polymerization proceeds by the ordinary radical mechanism with bimolecular termination.

Ethyl radicals are generated by the u.v. irradiation of ethylaluminum chlorides in toluene at -196°C (Ref. 12). The formation of these radicals is highly accelerated in the presence of a nitrile or carbonyl compound. The B group monomers in the alternating copolymerization have the same effect on ethylaluminum chlorides. Fig. 2 shows the promoting effect of methyl acrylate on the generation of ethyl radical from ethylaluminum sesquichloride in toluene. Styrene or other donor monomers may enhance the radical cleavage of ethylaluminum chlorides through a charge transfer interaction with the complex of a B group monomer and the aluminum component. Thus, the initiating species could come from ethyl radical of ethylaluminum chlorides.

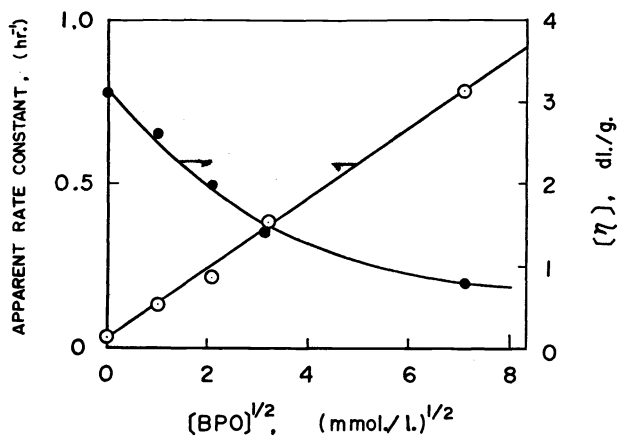


Fig. 1 Effect of BPO concentration on copolymerization of styrene and methyl acrylate with $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ in toluene.

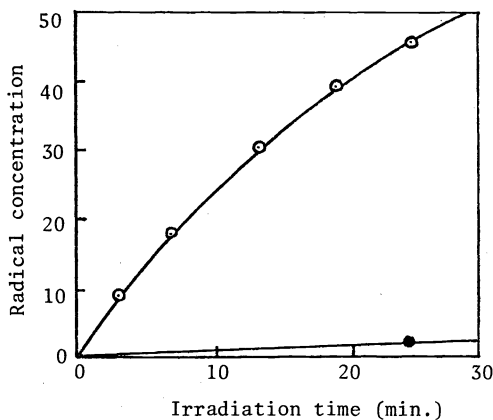


Fig.2 Ethyl radical from ethylaluminum sesquichloride in toluene by UV irradiation at -196°C (●) EASC 2mol dm^{-3}
(○) " + methyl acrylate 2.68 mol dm^{-3}

REACTION KINETICS AND ANOMALOUS PHENOMENA

The reaction kinetics were examined for the alternating copolymerization of styrene (St) and methyl acrylate (MA) with ethylaluminum sesquichloride (al) in toluene solution at 25°C and the rates of polymerization were expressed by the following equation:

$$R_p = k[\text{MA-al}]^{1.0}[\text{MA}_{\text{free}}]^0[\text{St}]^0 \quad (1)$$

in which MA-al represents the complex of methyl acrylate and ethylaluminum sesquichloride.

Thus, the rate of copolymerization does not depend on the concentration of styrene and uncomplexed methyl acrylate but only on the concentration of the complex.

Ethylboron chlorides (Ref. 13) are more effective catalysts than ethylaluminum chlorides in the alternating copolymerization of olefins and (meth)acrylic monomers as shown in Fig. 3 and the rate of polymerization remains constant throughout the course of reaction which means that the rate is independent of monomer concentration as above. These results indicate that the alternating copolymerizations are strongly dependent on the complex of B monomers and ethyl-aluminum or -boron chlorides.

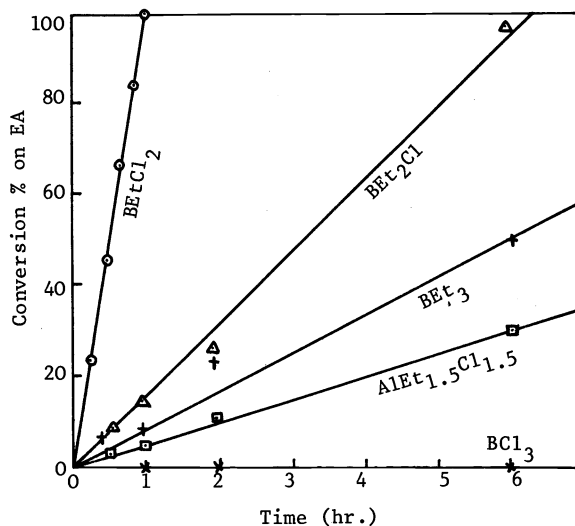


Fig. 3 Copolymerization of isobutylene and ethyl acrylate with metal halogenides in toluene at -20°C .

Further anomalous phenomena have been observed in the alternating copolymerizations. Table 1 shows the results of alternating copolymerization of "allyl resonance monomers" which strongly exhibit a tendency to degradative chain

TABLE 1. Copolymerization of allyl resonance monomers

Comonomers (g) A	Comonomers (g) B	Catalyst (mmol)	Solvent (ml.)	Time (min)	Yield (g)	$[\eta]$
Pr (80)	AN (2)	AlEtCl ₂ (50) ²	Toluene (30)	10	2.53	1.61
Pr (20)	MA (4)	"	-	"	1.64	4.95
IB (15)	AN (1.5)	AlEtCl ₂ (25) ²	n-C ₇ (20)	"	0.81	2.08
AC (15)	BA (3)	Al ₂ Et ₃ Cl ₃ (12.5) ³	"	300	2.48	0.38
ALAC	MA	"	"	50	1.32	solid

Pr = propylene, IB = isobutylene, AN = acrylonitrile, MA = methyl acrylate, BA = n-butyl acrylate, AC = allyl chloride, ALAC = allyl acetate.

Polymerization temperature: -78°C except 0°C of ALAC-MA.

transfer in conventional radical polymerization and are difficult to polymerize. In the alternating copolymerization systems with metal halogenides,

such degradative chain transfer hardly occurs and high molecular weight copolymers are easily obtained in high yields. This is quite contrary to the conventional radical polymerization.

Oxygen and hydroquinone, which are inhibitors in the conventional radical polymerization, promote or do not retard the reaction as shown in Table 2. Carbontetrachloride is a powerful chain transfer agent in the conventional radical polymerization but no chain transfer reaction was observed in this

TABLE 2. Effect of additives on the copolymerization of St and MA with $\text{AlEt}_{1.5}\text{Cl}_{1.5}$

No.	Additives	(mmol/dm ³)	Polymer Yield (g)	[η] (dl/g)
1.	-	-	1.65	2.84
2.	Oxygen	5% in N ₂ bubbling	3.04 ¹	1.77
3.	BPO	1.0	4.20	-
4.	Hydroquinone	12.5	1.51	3.97
5.	CCl ₄	4.0 x 10 ³	1.03	3.87 ²

25°C in toluene 60 min.

1. 40 min.

2. Beilstein test was negative.

alternating copolymerization. The mechanism of alternating copolymerization must explain these anomalous phenomena.

CHAIN TRANSFER REACTION

Chain transfer reactions are not completely absent from alternating copolymerizations but they usually occur only to a relatively small extent.

Fig. 4 shows the molecular weights of copolymers obtained in the alternating copolymerization of styrene and methyl acrylate with ethylaluminum sesquichloride in various solvents. The molecular weights of copolymers decrease proportionally with increasing chain transfer constants of solvents for the conventional radical polymerization but the slope of the line is rather small. This suggests that the alternating copolymerization with metal halogenides proceeds through a kind of radical species but the chain transfer activity of the growing chain end is specifically small.

Bamford et. al. (Ref. 14) observed a measurable chain transfer activity of carbon tetrabromide in the alternating copolymerization of styrene and methyl acrylate with ethylaluminum sesquichloride. The rate constant of chain transfer to styryl radical by carbon tetrabromide is, however, estimated to be approximately 43 times smaller than that of the chain transfer reaction without the complexing agent.

Lachinov et. al. (Ref. 15) studied the effect of zinc chloride on chain transfer reaction of carbon tetrabromide in radical polymerization of methyl methacrylate and found that the chain transfer constant and the rate constant of chain transfer decrease with increasing concentration of zinc chloride. The extrapolated value of the rate of chain transfer towards 1:1 molar ratio of zinc chloride and methyl methacrylate may be estimated to be ca. 40 times smaller than that for the uncomplexed system.

In conventional radical polymerizations, the chain transfer constants for a transfer agent vary widely according to the kinds of monomer radicals. The author (Ref. 4) pointed out that the chain transfer constants of carbon

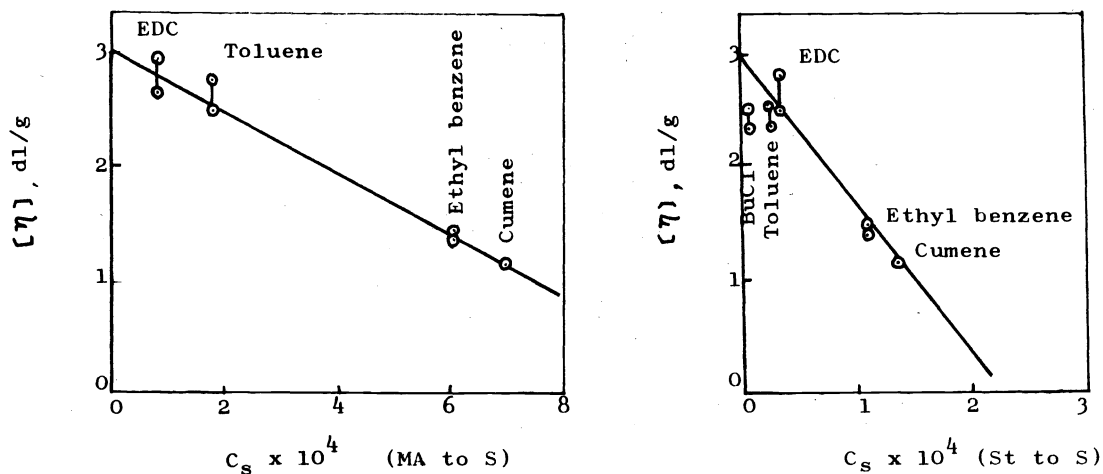


Fig.4 Molecular Weight Dependence on Solvent
in Polymerization of St and MA with EASC

tetrachloride are clearly separated into two groups of monomers in which donor monomers have fairly high values of the constant and acceptor monomers have very low values, and this classification coincides with that of A- and B-group monomers based on their behaviour in alternating copolymerization in the presence of Lewis acids.

Fuhrman et. al. (Ref. 16) expressed the rate constant for chain transfer by the following equation:

$$k_f = P_r Q_f \exp\{-e_r e_f\} \quad (2)$$

in which Q_f and P_r are resonance stabilization terms, and e_f and e_r are polar terms for the chain transfer agent and the growing radical, respectively. According to such extended treatment of Price-Alfrey's Q-e scheme, the donor monomers having low e -values show high activity towards a chain transfer agent and the acceptor monomers having high e -values exhibit rather inert nature, and the above difference of the chain transfer constants between two monomer groups is easily understood in terms of this equation. Further, when the group B acceptor monomers form complexes with Lewis acids, the greatly decreased reactivity in chain transfer is to be expected. Therefore, the considerable reduction of chain transfer reaction observed in the alternating copolymerization or homopolymerization with metal halogenides could be interpreted in such a way that the metal halogenide plays an important role at the growing chain end of the acceptor monomer by complexation.

EFFECT OF METAL HALIDES AND NATURE OF THE COMPLEXES

In conventional radical polymerizations, the effects of metal halides have been extensively investigated and the reaction mechanisms have been discussed. Bamford et. al. (Ref. 5) first determined the absolute rate constants in the polymerization of acrylonitrile in the presence of lithium chloride and revealed that the propagation constant is enhanced by lithium chloride while the termination reaction is not affected. They ascribed this phenomenon to complex formation at the growing acrylonitrile radical. In dimethylformamide, which was used as the solvent, lithium chloride is likely to have an ionic form and produces two kinds of complexes with acrylonitrile. The lithium cationic complex might lead to a decreased rate of propagation and the chlorine anionic complex may enhance the rate coefficient of propagation. This inference was supported by the experiments using lithium compounds with different anions.

Lachinov, Zubov and Kabanov (Ref. 17) determined absolute rate constants for

methyl methacrylate polymerization in the presence of aluminum bromide. The propagation rate constant is enhanced by AlBr_3 in the range of lower concentrations and decreased at the higher concentrations. In the latter range, the termination constant markedly decreased to the value of $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the order of 10^7 .

Bamford and Brumby (Ref. 18) examined the effect of aluminum chloride on the methyl methacrylate polymerization and found that commercial aluminum chloride considerably enhanced the rate of polymerization while pure AlCl_3 was much less effective. This means that the impurities in AlCl_3 greatly participate in the enhancement of the rate.

In order to compare the alternating copolymerization system with conventional radical polymerization, the author carried out the polymerization of methyl acrylate with azobisisobutyronitrile in toluene in the presence of ethylaluminum sesquichloride at various concentrations. The results shown in Fig.5 exhibit rather high retardation of ethylaluminum sesquichloride even in the lower range of concentrations. This is likely to explain the substantial lack of homo-propagation in the alternating copolymerization with ethylaluminum chlorides.

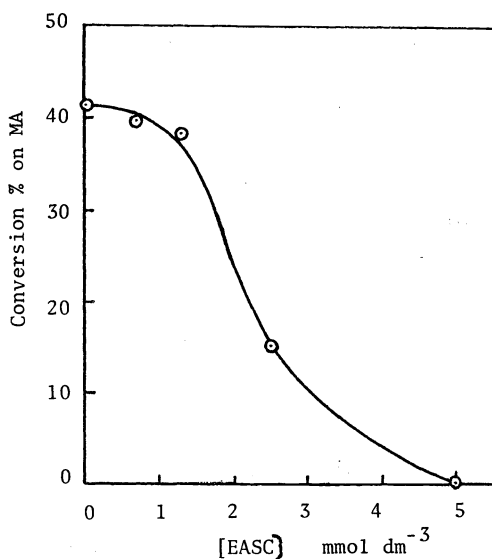


Fig.5 Effect of ethylaluminum sesquichloride on radical polymerization of methyl acrylate at 67°C, MA 834 mmol dm⁻³ in toluene
AIBN 2 mmol dm⁻³

In the alternating copolymerization of styrene and methyl acrylate with ethylaluminum chlorides, ethylaluminum chlorides form stable complexes with methyl acrylate which are estimated as 1:1 complex by cryoscopic measurements. The charge transfer absorption of the complexes with ethylaluminum chlorides was observed at 290nm in u.v. spectra. The equilibrium constant for formation of the complex with $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ was estimated to be more than $40 \text{ mol}^{-1} \text{ dm}^3$ at 25°C.

The interaction between styrene and the binary complex of methyl acrylate and the aluminum component, however, seems to be so weak that it can be hardly detected by u.v. spectrometry and there may be only a kind of contact type charge transfer interaction. In other alternating copolymerization systems, however, such ternary complexes between two monomers and metal halogenides have been detected at low temperatures, e.g. in the system of butadiene and acrylonitrile with ethylaluminum dichloride by Furukawa et. al. (Ref. 19) and in the system of styrene and methyl methacrylate with tin tetrachloride by Hirai et. al. (Ref. 20). Hirai and Komiyama have intensively investigated the structure and equilibrium constant of the ternary complex of styrene, methyl methacrylate and tin tetrachloride. The equilibrium constant was determined

to be 0.60 at -40°C in n-hexane (Ref. 21). The structure of the ternary complex was considered to be rather unstable and to have a statistical time-averaged conformation (Ref. 22).

MECHANISM OF ALTERNATING REGULATION

Three different kinds of mechanism to explain alternating regulation have been postulated for alternating copolymerizations in the presence of metal halogenides and the mechanism has not yet been settled. One is the cross-propagation mechanism based on the conventional radical copolymerization scheme derived from Lewis-Mayo equation in which the alternating regulation is ascribed to the selective cross-propagation reactions enhanced by the complex formation of the acceptor monomer with the metal halogenide and two kinds of monomer radicals appear in the course of copolymerization (Refs. 23, 24).

A second is the monomer complex mechanism in which a ternary molecular complex between two monomers and the metal halogenide is involved and acts as if it were a single monomer and is selectively polymerized to give an alternating copolymer (Refs. 25-29).

The third one is the radical complex mechanism in which the charge transfer interaction between the growing chain end, the attacking monomers and metal halogenide governs the alternating regulation and the metal halogenide plays an important role on site (Refs. 10, 30).

It is certain that the alternating copolymerization with metal halogenides is a kind of radical polymerization. Most of the features must be described by a conventional radical mechanism in which modifications are introduced to allow for the existence of charge transfer interactions between the reactants, especially at the growing chain ends.

Bamford and Brumby (Ref. 31) first revealed and discussed the effect of solvent on the absolute rate coefficients for propagation in conventional radical polymerizations. Recently, Kamachi et. al. (Refs. 32, 33) have studied this subject in more detail and reached the conclusion that a kind of radical complex is formed with solvent and this affects the propagation reaction. In the alternating copolymerizations, charge transfer interaction between the radical and monomers may become more important. Already, Walling et. al. (Ref. 34) ascribed the alternating regulation in styrene/maleic anhydride copolymerization to a kind of charge transfer interaction between the radical and the attacking monomer.

Effects of metal halides on the radical polymerization have been extensively discussed so far. The role of metal halide at the growing chain end seems to be important. Zubov et. al. (Ref. 35) suggested that poly(methyl methacrylate) radicals form complexes with aluminum halides to cause enhanced rate of propagation and proposed it as "radical coordination polymerization". Golubev et. al. (Ref. 36) indicated that the metal halides form complexes with the radical more strongly than with the monomers.

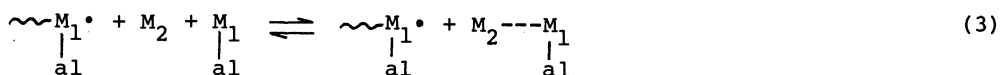
In the alternating copolymerization of styrene and methyl acrylate with ethylaluminum sesquichloride, the polymer is produced in homogeneous solution in toluene. But the complex of polymer with ethylaluminum chlorides is insoluble in toluene. This precipitate is quickly dissolved by the addition of small amount of methyl acrylate. This means that the aluminum component forms much stronger complex with acrylate monomer than with polymer. Such observations lead us to infer that the acrylate radical having an sp^2 orbital at the conjugated position of the carbonyl group forms a complex with aluminum component more strongly than the internal acrylate unit in the copolymer.

The chain transfer reaction gives us further information about the reactivity of the growing radical. The chain transfer reactions were observed to be much reduced in the presence of metal halogenides as shown before. This should be ascribed to the inert nature of the radical due to complexation with metal halogenides. The inefficiency of chain transfer reagents observed in alternating copolymerizations suggests that the complexed radicals may be predominant species in the course of polymerization probably all radical species being complexed.

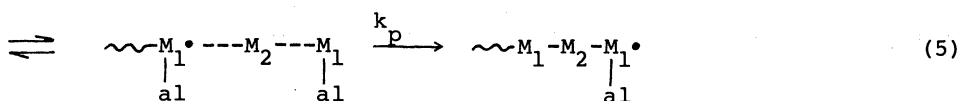
The fact that the degradative chain transfer reaction of allyl resonance monomers is hardly observed in the alternating copolymerizations is understandable in terms of the inert nature of the complexed radicals.

Ternary complexes comprising two monomers and a metal halogenide were observed to be rather unstable. According to Hirai's observations, the ternary complex shows a single time-averaged line on NMR spectra which indicates rapid exchange of monomers between the complexed state and uncomplexed state (Ref. 21). Thus, the life time of the ternary complex could be less than $10^{-3} \sim 10^{-5}$ sec. which is shorter than the life time of radicals per propagation step in conventional radical polymerizations, 10^{-2} sec.

In the alternating copolymerization of two monomers, M_1 and M_2 , which alkyl-aluminum halide (al), the general scheme of the propagation steps is expressed as follows:

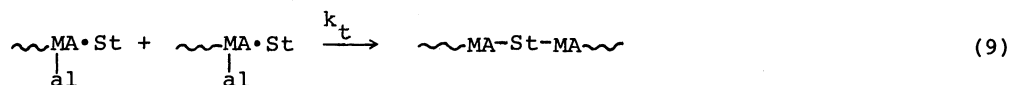
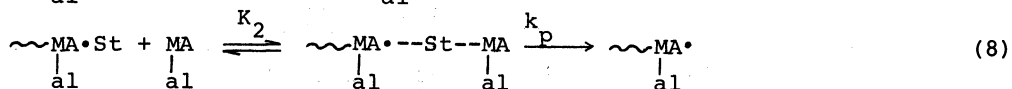


(III)



(IV)

If the ternary complex (II) were of longer life than the growing radical, the propagation step could be considered to proceed mainly through reactions (3) and (5). As the ternary complexes are estimated to be rather unstable, however, the polymerization should be generally regarded to proceed through reactions (4) and (5). Thus, the kinetic scheme of alternating copolymerization of styrene (St) and methyl acrylate (MA) is likely to be:

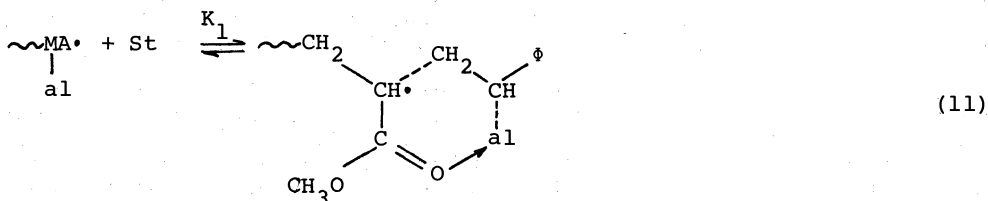


In the stationary state, the rate of polymerization R_p derived from this scheme is:

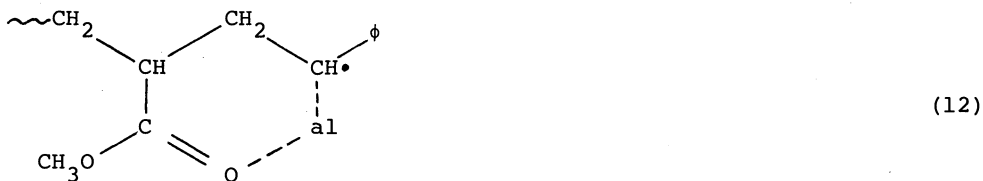
$$R_p = 2k_p [\text{MA}] \left(\frac{\mathcal{J}}{k_t} \right)^{\frac{1}{2}} \quad (10)$$

This relation is the same as the kinetic equation (1) deduced from the experimental results.

The equilibrium reaction (7) can be expressed in a resonance form:



In the alternative scheme, the complexed radical resulting from the reaction of $\sim\text{MA}\cdot + \text{St}$ could have the structure (Ref. 14):



To clarify in more detail the mechanism of alternating regulation, the determination of absolute rate coefficients in the alternating copolymerization must be more informative. Such trials have just started (Refs. 11, 14); so far the values of k_p/k_t have been observed to be extraordinarily large compared with those in conventional radical homopolymerizations.

For a long time, the mechanism of alternating regulation has remained unclear. Recent approaches, however, may be expected to solve some of the problems.

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