Effects of Complexing Agents in
Radical Copolymerization*

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Synopsis

Radical copolymerization of methyl methacrylate (MMA, M_1) with various monomers has been studied in presence of modifiers, i.e., complexing agents (CA): $ZnCl_2$, $AlCl_3$, $AlBr_3$, $Al(C_2H_5)_2Cl$, forming coordinate complexes with ester group of the monomer and of the propagating radical. The comonomers of the first group form complexes of similar structure and stability as MMA, methyl acrylate, or butyl acrylate. The comonomers of the second group do not form complexes with the modifiers (vinylidene chloride, 2,6-dichlorostyrene, p-chlorostyrene, styrene). For all systems studied the copolymer composition follows the Mayo-Lewis equation. In the first group of the systems the effective reactivity ratios (r_1, r_2) approach unity with increase of the CA molar content ($r_1 = r_2 \simeq 1$ at $[CA]/[MMA] + [MA] \geq 0,3$) In the second group of the systems the values of r_1 either increase to a limit value (at $[CA]/[MMA] \geq 0.3$), pass through maximum, or decrease to a limiting value with the CA molar content. The values of r_2 decrease in all systems. The character of variation of r_1 and r_2 has been explained in terms of effects of the CA's on reactivity of MMA and PMMA radical. The equations for the copolymer compositions in these systems have been derived.

The salts of nontransition metals (LiCl, $MgCl_2$, $ZnCl_2$, $AlCl_3$, $AlBr_3$) forming complexes with functional groups of vinyl monomers considerably effect the rate of radical polymerization and composition of the copolymers.[1-12] The present paper deals with the studies of the mechanism of these processes. For this purpose methyl methacrylate (MMA), a monomer having a functional group can interact with the complexing agents (CA) like $ZnCl_2$, $AlBr_3$, $Al(C_2H_5)_2Cl$, was copolymerized with other monomers of different types. In the first group of the systems, the comonomers form complexes of similar structure and stability as MMA [methyl acrylate (MA), butyl acrylate (BA)]. The ability to form complexes in the second group of comonomers [vinylidene chloride (VDC), styrene (St), p-chlorostyrene (p-CST), and 2,6-dichlorostyrene (2,6-DCST)] is much lower than that of MMA.

EXPERIMENTAL

The monomers were purified according to accepted techniques, then carefully dried first over metallic calcium and then over calcium hydride

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in vacuo. AlBr$_3$ was purified by multiple vacuum distillation, AlCl$_3$ by multiple distillation in argon atmosphere. ZnCl$_2$ and Al(C$_2$H$_5$)$_2$Cl were reagent grade materials and were used without further purification. The criterion of purity of the reagents was formation of colorless complex on mixing of the monomers with the complexing agents. The mixing was carried out in an all-glass apparatus *in vacuo.* Polymerization was initiated either photochemically (λ = 313 mμ) or by thermal decomposition of azobisisobutyronitrile (AIBN). Preparation of the reaction systems was carried out in the dark because in some of the systems diffusing light causes polymerization to occur. In the dark, the uninitiated reaction was not observed. The polymerization rates were measured dilatometrically and gravimetrically. The polymers were separated from the complexing agents by pouring the reaction mixture into a mixture of methanol and hydrochloric acid and then reprecipitated several times. Compositions of the copolymers MMA–VDC, MMA–*p*-CST and MMA–2,6-DCST were determined by analysis for chlorine by Schöniger's method.[13] The composition of MMA–MA copolymers was determined by means of infrared spectroscopy by the ratio of optical densities of deformation modes of CH$_3$– and –CH$_2$– groups[14] at 1486 and 1451 cm^{-1} and the composition of the MMA–BA copolymers by a NMR method based on the ratio of the areas under the peaks of —O—CH$_3$ and —O—CH$_2$— protons.[15] The compositions of the MMA–St copolymers were determined by elementary analysis and from the NMR spectra on the basis of the ratio of the areas under the peaks of benzene ring protons to the total area under the spectrum.[16] The NMR spectra were recorded on a NMR spectrometer (JNM-C-60-HL, JEOL) in 8% solution in CCl$_4$ and in 6% solutions of the MMA–BA copolymers in CHCl$_3$.

In all cases the dependence of the copolymer composition on the composition of the feed formally obeyed Mayo-Lewis' equation. The copolymerization reactivity ratios (r_1, r_2) were determined by graphical[17] and analytical[18] methods.

RESULTS

Compositions of the MMA–MA copolymers prepared in the presence of ZnCl$_2$ and AlBr$_3$ approach the composition of the monomeric mixture with increase of the complexing agent (CA) content in the reaction system and become practically equal to it at comparatively small CA content, i.e.; [CA]/[MMA] + [MA] $\geq$ 0.2-0.3), when a considerable fraction of the monomer molecules is still uncomplexed. In other words, the apparent copolymerization reactivity ratios become equal to unity and remain unchanged at further increase of CA concentration (Table I, Fig. 1). A similar result has been observed in the MMA–BA system (Table I). Establishment of the limit values of the copolymerization constants at [CA]/[M$_1$] + [M$_2$]) $\simeq$ 0.2-0.3 indicates that above this ratio practically all the propagation occurs by a mechanism involving CA participation.

TABLE I.   Copolymerization of MMA (M_1) with MA and BA in Presence of CA's

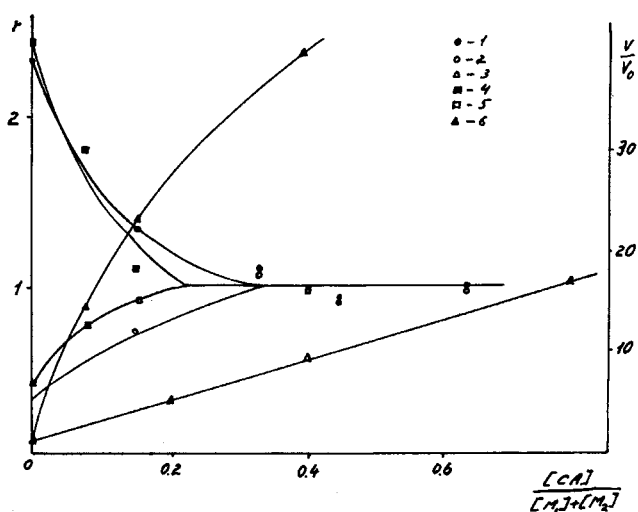| CA	M_2	Polymerization conditions	$\dfrac{[CA]}{[M_1]+[M_2]}$	M_2 (mole fraction) in the monomer mixture	m_2 in the co-polymer	r_1	r_2
ZnCl₂	MA	[AIBN] =	0	0.10	0.05		
		5 × 10⁻³		0.20	0.10		
		mole/l.,		0.25	0.13	2.23 ±	0.36 ±
		50°C		0.30	0.16	0.13	0.1
				0.40	0.23		
				0.50	0.32		
			0.15	0.10	0.08		
				0.20	0.16		
				0.30	0.24	1.33 ±	0.70 ±
				0.40	0.32	0.03	0.03
				0.50	0.43		
				0.60	0.53		
			0.33	0.10	0.09		
				0.20	0.19		
				0.30	0.29	1.11 ±	1.09 ±
				0.40	0.40	0.10	0.12
				0.50	0.50		
			0.45	0.10	0.11		
				0.20	0.20		
				0.30	0.30	0.91 ±	0.88 ±
				0.40	0.39	0.03	0.09
				0.50	0.49		
			0.64	0.10	0.11		
				0.20	0.20		
				0.30	0.30	0.99 ±	0.93 ±
				0.40	0.41	0.05	0.1
				0.50	0.50		
AlBr₃	MA	UV (λ = 313		0.10	0.05		
		mμ), 48°C		0.20	0.10	2.30 ±	0.45 ±
				0.30	0.16	0.15	0.15
				0.50	0.31		
			0.075	0.10	0.06		
				0.20	0.13		
				0.30	0.20	1.75 ±	0.78 ±
				0.40	0.29	0.04	0.05
				0.50	0.40		
			0.15	0.10	0.09		
				0.20	0.19	1.11 ±	0.91 ±
				0.30	0.28	0.04	0.10
				0.50	0.48		
			0.40	0.10	0.11		
				0.20	0.20	0.96 ±	0.96 ±
				0.30	0.30	0.05	0.11
				0.50	0.51		
ZnCl₂	BA	[AIBN] =	0	0.40	0.25		
		5 × 10⁻³	0.15	0.40	0.33		
		mole/l.,	0.33	0.40	0.35		
		50°C	0.45	0.40	0.39		

Fig. 1. Dependence of the copolymerization parameters and relative copolymeriza-
tion rate (V/V_0) where V_0 is the rate of polymerization without CA in the system
MMA(M_1)–MA in presence of CA's on the ratio [CA]/([MMA] + [MA]): (1) r_1,
(2) r_2, and (3) V/V_0 at [MMA]:[MA] = 1:1, 50°C, [AIBN] = 5 × 10^{-3} mole/1.,
CA = $ZnCl_2$; (4) r_1, (5) r_2, and (6) V/V_0 at [MMA]:[MA] = 1:1, 48°C, UV (λ =
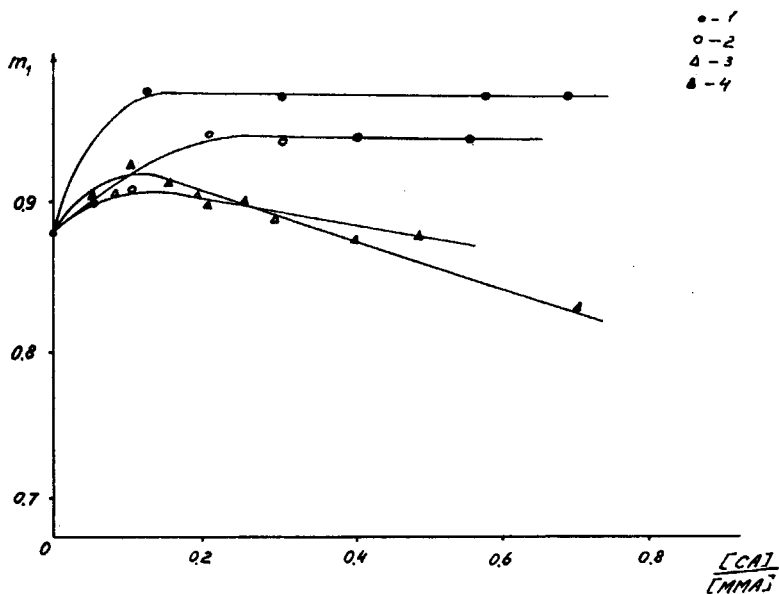313mμ), CA = $AlBr_3$.

Fig. 2. Dependence of MMA content in MMA–VDC copolymer on the ratio [CA]/-
[MMA]: (1) CA = $ZnCl_2$, 50°C, [AIBN] = 5 × 10^{-3} mole/l; (2) CA = $Al(C_2H_5)_2Cl$,
UV(λ = 313mμ), 20°C; (3) CA = $AlBr_3$, UV (λ = 313mμ), 20°C; (4) CA = $AlCl_3$, UV
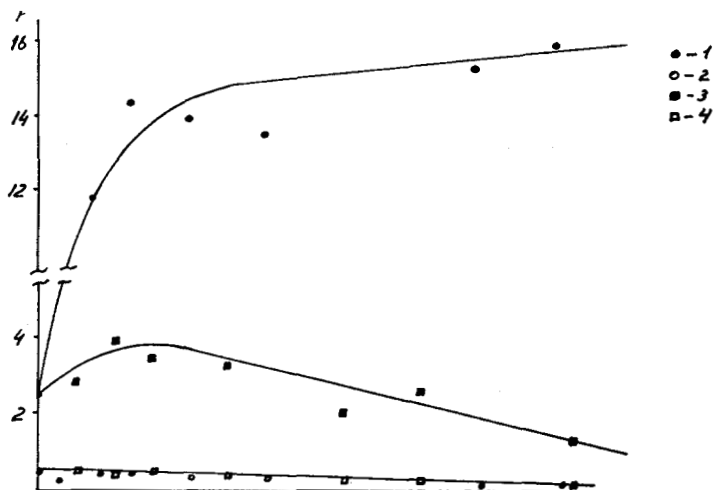(λ = 313mμ), 20°C.

Fig. 3. Dependence of the copolymerization parameters in system MMA(M_1)–VDC on the ratio [CA]/[MMA]: (1) r_1 and (2) r_2 at 50°C, [AIBN] = 5 × 10^{-3} mole/l., CA = ZnCl$_2$; (3) r_1 and (4) r_2 at 20°C, UV (λ = 313mμ), CA = AlCl$_3$.

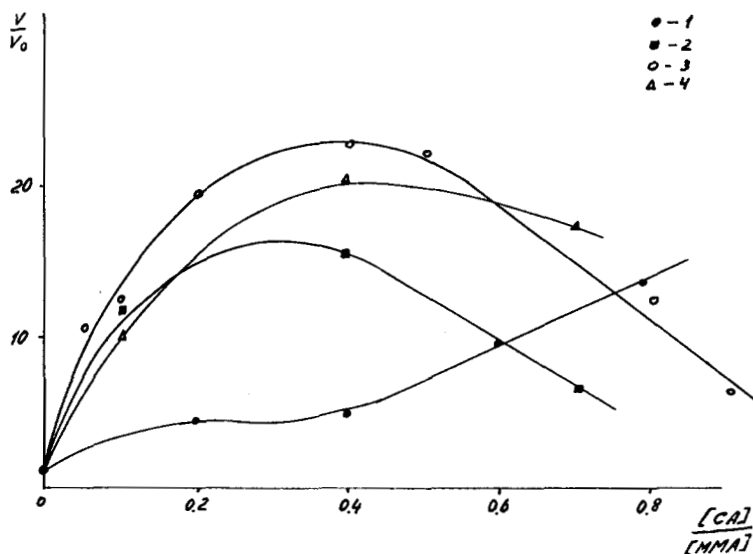Fig. 4. Dependence of the relative copolymerization rate in system MMA–VDC on the ratio [CA]/[MMA]: (1) [MMA]:[VDC] = 2:1, CA = ZnCl$_2$; (2) [MMA]:[VDC] = 10:1, CA = AlCl$_3$; (3) [MMA]:[VDC] = 3:1, CA = AlCl$_3$; (4) [MMA]:[VDC] = 1:1, CA = AlCl$_3$.

Figure 1 also shows the relative rates of the copolymerization in the MMA–MA (1:1) system. In the region of the smaller CA content, the change in relative rate is paralleled by a change in the copolymerization constants. At higher CA contents, the copolymerization rates continue to

TABLE II
Copolymerization of MMA (M_1) with VDC in Presence of CA's

CA	Polymerization conditions	M_2 (mole fraction) $\frac{[CA]}{[MMA]}$	in monomer mixture	m_2 in co-polymer	r_1	r_2
ZnCl$_2$	[AIBN] = 5 × 10^{-3} mole/l., 50°C	0	0.10	0.05		
			0.17	0.08		
			0.25	0.12		
			0.29	0.14	2.54 ± 0.20	0.5 ± 0.15
			0.30	0.15		
			0.33	0.17		
			0.50	0.30		
		0.03	0.10	0.02		
			0.20	0.04		
			0.30	0.08	5.3 ± 0.4	0.18 ± 0.17
			0.45	0.14		
			0.55	0.21		
		0.07	0.10	0.01		
			0.20	0.02		
			0.30	0.04	11.8 ± 0.8	0.41 ± 0.22
			0.40	0.07		
			0.45	0.08		
		0.12	0.20	0.01		
			0.25	0.03		
			0.29	0.03	14.5 ± 2.5	0.4 ± 0.2
			0.38	0.04		
			0.50	0.09		
		0.20	0.10	0.01		
			0.20	0.01		
			0.30	0.03	13.9 ± 0.9	0.21 ± 0.07
			0.40	0.05		
			0.45	0.07		
		0.30	0.20	0.02		
			0.25	0.02		
			0.29	0.03	13.5 ± 2.4	0.3 ± 0.2
			0.33	0.04		
			0.50	0.10		
		0.57	0.20	0.02		
			0.25	0.02		
			0.29	0.03	15.7 ± 1.2	0.1 ± 0.2
			0.33	0.04		
			0.50	0.08		
		0.68	0.20	0.02		
			0.25	0.02		
			0.29	0.03	16.0 ± 3.0	0.2 ± 0.2
			0.33	0.04		
			0.50	0.09		

TABLE II (*continued*)
Copolymerization of MMA (M_1) with VDC in Presence of CA's

CA	Polymerization conditions	M_2 (mole fraction) $\dfrac{[CA]}{[MMA]}$	in monomer mixture	m_2 in co-polymer	r_1	r_3
AlCl$_3$	UV (λ = 313 mμ), 20°C	0	0.09	0.04		
			0.25	0.12		
			0.40	0.21	2.5 ±	0.4 ±
			0.50	0.29	0.1	0.05
			0.60	0.37		
			0.75	0.54		
		0.05	0.15	0.06		
			0.28	0.13	2.82 ±	0.54 ±
			0.45	0.24	0.06	0.04
			0.65	0.44		
		0.10	0.09	0.03		
			0.25	0.07		
			0.40	0.12	4.0 ±	0.16 ±
			0.50	0.18	0.2	0.08
			0.60	0.26		
			0.75	0.41		
		0.15	0.13	0.04		
			0.25	0.09	3.5 ±	0.52 ±
			0.50	0.25	0.3	0.06
			0.65	0.39		
		0.25	0.13	0.04		
			0.25	0.10	3.3 ±	0.37 ±
			0.50	0.24	0.2	0.09
			0.65	0.37		
		0.40	0.08	0.04		
			0.25	0.13		
			0.40	0.21	2.02 ±	0.13 ±
			0.50	0.27	0.07	0.03
			0.60	0.34		
			0.75	0.44		
		0.50	0.13	0.05		
			0.25	0.11	2.6 ±	0.22 ±
			0.50	0.23	0.1	0.03
			0.65	0.37		
		0.70	0.09	0.07		
			0.25	0.17		
			0.40	0.22	1.32 ±	0.05 ±
			0.50	0.32	0.18	0.06
			0.60	0.37		
			0.75	0.46		

increase despite the constancy of r_1 and r_2. The increase in the rate in the region of high $[CA]/[M_1] + [M_2])$ ratios is probably due to a decrease of the termination constants similarly as described by Lachinov et al.[19]
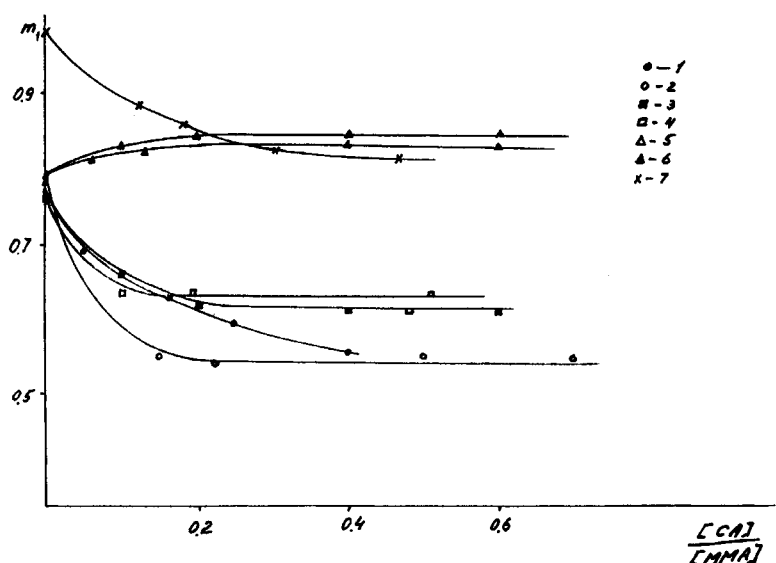
Fig. 5. Dependence of MMA content in the MMA(M_1) copolymers on the ratio [CA]/[MMA]: (1) M_2 = St, [M_1]:[M_2] = 5.67, CA = $ZnCl_2$, [AIBN] = 5 × 10^{-3} mole/l.. 50°C; (2) M_2 = St, [M_1]:[M_2] = 3.0, CA = Al $(C_2H_5)_2$ Cl, UV (λ = 313mμ), 20°C; (3) M_2 = p-CSt, [M_1]:[M_2] = 5.67, CA = $ZnCl_2$, [AIBN] = 5 × 10^{-3} mole/l., 50°C; (4) M_2 = p-CSt, [M_1]:[M_2] = 5.67, CA = Al$(C_2H_5)_2$Cl, UV, (λ = 313mμ), 20°C; (5) M_2 = 2,6-DCSt, [M_1]:[M_2] = 1.28, CA = $ZnCl_2$, [AIBN] = 5 × 10^{-3} mole/l., 50°C; (6) M_2 = 2,6-DCSt, [M_1]:[M_2] = 1.5, CA = Al$(C_2H_5)_2$Cl, UV (λ = 313mμ), 20°C; (7) M_2 = 2,6-DCSt, [M_1]:[M_2] = 5.57, CA = AlCl$_3$, UV (λ = 313mμ), 20°C.

Figure 2 shows the dependence of the copolymer composition in the system MMA(M_1)–VDC at fixed monomer mixture composition (MMA: VDC = 3:1) on CA content. One can see that the effects depend on the nature of CA. Introduction of $ZnCl_2$ and Al$(C_2H_5)_2$Cl brings about an increase of MMA content in the copolymer, which attains a constant value at [CA]/[MMA] = 0.2–0.3. But in the case of aluminum halides, the MMA content in the copolymer first increases and then decreases, passing through a maximum. The apparent values of r_1 and r_2 for the typical systems MMA–VDC–$ZnCl_2$ and MMA–VDC–AlCl$_3$ are shown in Table II and in Figure 3. As can be seen, r_1 similarly increases and then either remains constant ($ZnCl_2$) or decreases (AlCl$_3$) with CA content; r_2 decreases in the whole range of CA concentrations. The nonlinear character of r_1 variation with $ZnCl_2$ content in the system MMA–VDC–$ZnCl_2$ shows that linear extrapolation of the results obtained at low [$ZnCl_2$] to the 1:1 complex, based on the assumption that the only effect of $ZnCl_2$ is activation of MMA,[4] is invalid.

The character of r_1 variation indicates that in these systems all additions to MMA radicals also occur with CA participation a CA concentrations lower than stoichiometric (Fig. 4). At low CA content, the copolymeri-
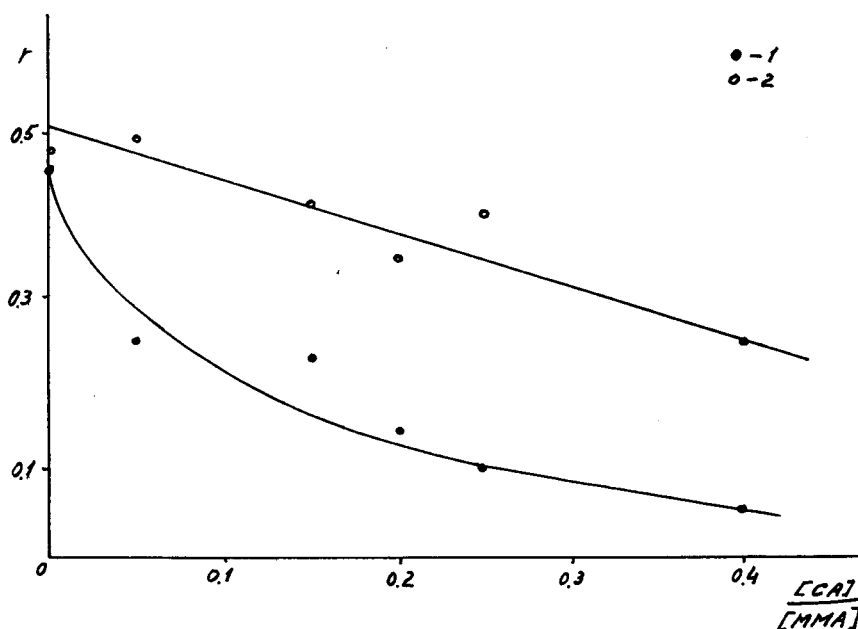
Fig. 6. Dependence of the copolymerization parameters in system MMA(M_1)-St on the ratio [CA]/[MMA]. I-r_1, 2-r_2, [AIBN] = $5 \cdot 10^{-3}$ mole/l., t = 50°C, CA = $ZnCl_2$.

zation rates are changed (increased) in a parallel way with r_1. In the region of high CA content the copolymerization rates are either decreased, though at somewhat higher CA concentrations than r_1 is decreased (when CA is $AlCl_3$) or continuously increased (when CA is $ZnCl_2$). The difference again is probably due to the effects of CA on termination constants.

In order to clarify further the mechanism of the process it was also of interest to investigate the role of the nature of the second monomer on the parameters of radical copolymerization in presence of CA. The copolymerization of MMA with styrene, p-chlorostyrene and 2,6-dichlorostyrene as the monomers of the similar structure but different polarization of the double bond has been studied. The e values for St and p-CST are equal to -0.8 and -0.3, respectively.[20] The accepted e value for 2,6-DCSt is ~ 0.1 (close to the value of 2,5-dichlorostyrene), because calculation from the copolymerization constants in the system MMA(M_1)-2,6-DCSt (r_1 = 2.05, r_2 = 0.12) gives too high a value (e_2 = $+2$) due to steric hindrance in' homopropagation for 2,6-DCSt,[21] which are not taken into account in the Q–e scheme.

Figure 5 shows the dependence of the copolymer composition for the monomer pairs MMA–St, MMA–p-CSt, and MMA–2,6-DCSt on CA concentration at fixed composition of the feed. In the systems MMA–2,6-DCSt–$ZnCl_2$ and MMA–2,6-DCSt–Al(C_2H_5)$_2$Cl, the molar MMA content in the copolymer increases with an increase in CA concentration; in the other systems [MMA–St–$ZnCl_2$, MMA–St–Al(C_2H_5)$_2$Cl, MMA–

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TABLE III
Copolymerization of MMA(M_1) with St in Presence of $ZnCl_2$

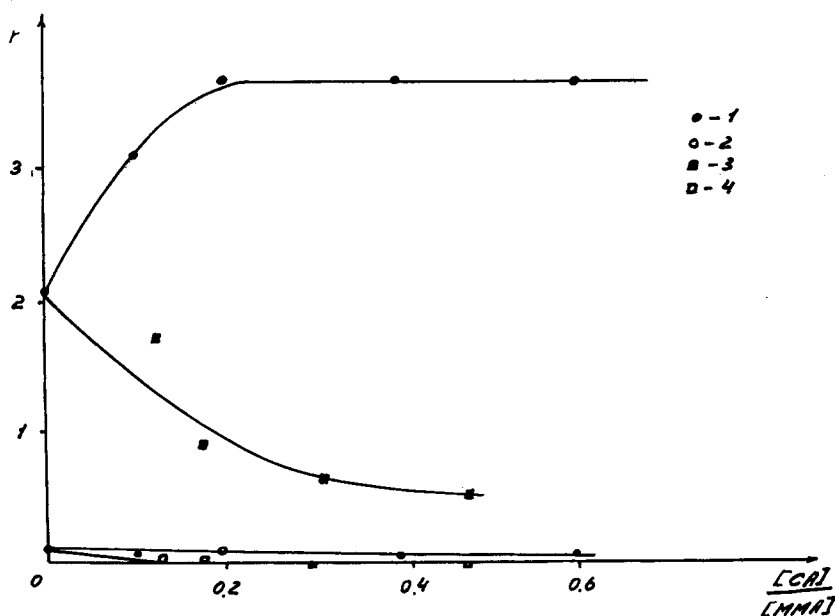| Polymerization conditions	$\dfrac{[ZnCl_2]}{[MMA]}$	M_2 (mole fraction) in monomer mixture	m_2 in copolymer	r_1	r_2	r_1r_2
[AIBN] = 5×10^{-3} mole/l., 50°C	0	0.05	0.10			
		0.10	0.18			
		0.15	0.23			
		0.20	0.27			
		0.25	0.33	0.45 ± 0.01	0.47 ± 0.03	0.212
		0.29	0.35			
		0.40	0.43			
		0.50	0.50			
		0.65	0.61			
		0.70	0.64			
	0.05	0.05	0.15			
		0.10	0.25			
		0.15	0.31	0.25 ± 0.02	0.49 ± 0.03	0.122
		0.65	0.61			
		0.70	0.67			
	0.15	0.05	0.26			
		0.10	0.31			
		0.15	0.37	0.23 ± 0.05	0.41 ± 0.1	0.094
		0.65	0.63			
		0.70	0.65			
	0.20	0.14	0.36			
		0.20	0.39			
		0.25	0.45	0.15 ± 0.02	0.37 ± 0.06	0.056
		0.29	0.45			
		0.40	0.50			
		0.50	0.54			
	0.25	0.05	0.26			
		0.10	0.35			
		0.15	0.41	0.10 ± 0.01	0.40 ± 0.08	0.040
		0.65	0.61			
		0.70	0.63			
	0.40	0.05	0.36			
		0.10	0.42			
		0.14	0.45			
		0.15	0.45			
		0.20	0.44	0.056 ± 0.003	0.25 ± 0.03	0.014
		0.25	0.47			
		0.29	0.49			
		0.50	0.55			
		0.65	0.59			
		0.70	0.61			

Fig. 7. Dependence of the copolymerization parameters in the system MMA(M_1)–2,6-DCSt on the ratio [CA]/[MMA]: (1) r_1 and (2) r_2 at CA = ZnCl$_2$, [AIBN] = 5 × 10^{-3} mole/l., 50°C; (3) r_1 and (4) r_2 at CA = AlCl$_3$, UV (λ = 313 mμ), 20°C.

p-CST–ZnCl$_2$, MMA–2,6-DCSt–AlCl$_3$] it decreases. Despite the differences in the direction of the changes of the copolymer compositions, in all cases the latter approach limiting values at relatively low CA content.

Attempts to copolymerize MMA with St and p-CSt in presence of aluminum halides failed because these compounds cause fast cationic polymerization of St and p-CSt even in the presence of an excess of MMA.

The copolymerization parameters have been determined in the characteristic systems MMA–St–ZnCl$_2$, MMA–2,6-DCSt–ZnCl$_2$, and MMA–2,6-DCSt–AlCl$_3$ (MMA = M_1, see Tables III and IV and Figs. 6 and 7).

The r_1 and r_2 are in MMA–St system decrease with decreasing ZnCl$_2$ and the product r_1r_2 becomes very low; this is usually related to a high alternating tendency in the copolymer. The structure of the copolymers has been checked by means of NMR. Figure 8 shows the spectra of the copolymers prepared in presence of ZnCl$_2$ (Fig. 8a) and Al(C$_2$H$_5$)$_2$Cl (Fig. 8b). For the sake of comparison NMR spectra of the practically alternating copolymer prepared[11] in presence of Al(C$_2$H$_5$)$_{1.5}$Cl$_{1.5}$ (Fig. 8c) and of a conventional radical copolymer (Fig. 8d) are reproduced. All the copolymers have 1:1 composition. As can be seen from Figure 8, the spectra of the copolymers prepared with ZnCl$_2$ and Al(C$_2$H$_5$)Cl differ from the conventional random copolymer and show characteristic splitting of the α-methyl and methoxyl protons similar to that in the alternating copolymer. The copolymerization rates are strongly increased with ZnCl$_2$ in the system (Fig. 9).

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TABLE IV
Copolymerizarion of MMA (M_1) with 2,6-DCSt in Presence of CA's

CA	Polymerizarion conditions	$\frac{[CA]}{[MMA]}$	M_2 in monomeric mixture	min_2 copolymer	r_1	r_2
ZnCl$_2$	[AIBN] =	0	0.20	0.10		
	5 × 10^{-3}		0.28	0.13	2.05 ±	0.12 ±
	mole/l., 50°C		0.33	0.15	0.04	0.02
			0.44	0.21		
		0.1	0.20	0.07		
			0.28	0.10	3.10 ±	0.05 ±
			0.33	0.12	0.24	0.01
			0.44	0.17		
		0.2	0.20	0.06		
			0.28	0.09	3.72 ±	0.09 ±
			0.33	0.11	0.04	0.01
			0.44	0.16		
		0.4	0.20	0.06		
			0.28	0.09	3.68 ±	0.09 ±
			0.33	0.11	0.1	0.03
			0.44	0.16		
		0.6	0.20	0.06		
			0.28	0.09	3.68 ±	0.09 ±
			0.33	0.11	0.1	0.03
			0.44	0.16		
AlCl$_3$	UV (λ = 313	0.126	0.15	0.11		
	mμ), 20°C		0.21	0.16	1.76 ±	0.42 ±
			0.47	0.32	0.44	0.30
			0.60	0.35		
		0.18	0.16	0.15		
			0.26	0.23	0.89 ±	−0.04 ±
			0.46	0.36	0.12	0.24
			0.62	0.35		
		0.31	0.15	0.18		
			0.28	0.24	0.62 ±	−0.18 ±
			0.49	0.34	0.07	0.17
			0.56	0.37		
		0.47	0.15	0.19		
			0.40	0.35	0.49 ±	−0.30 ±
			0.52	0.22	0.16	0.17
			0.60	0.38		

TABLE V
Effects of CA on C=O Band in the Infrared Spectrum of the MMA Complex

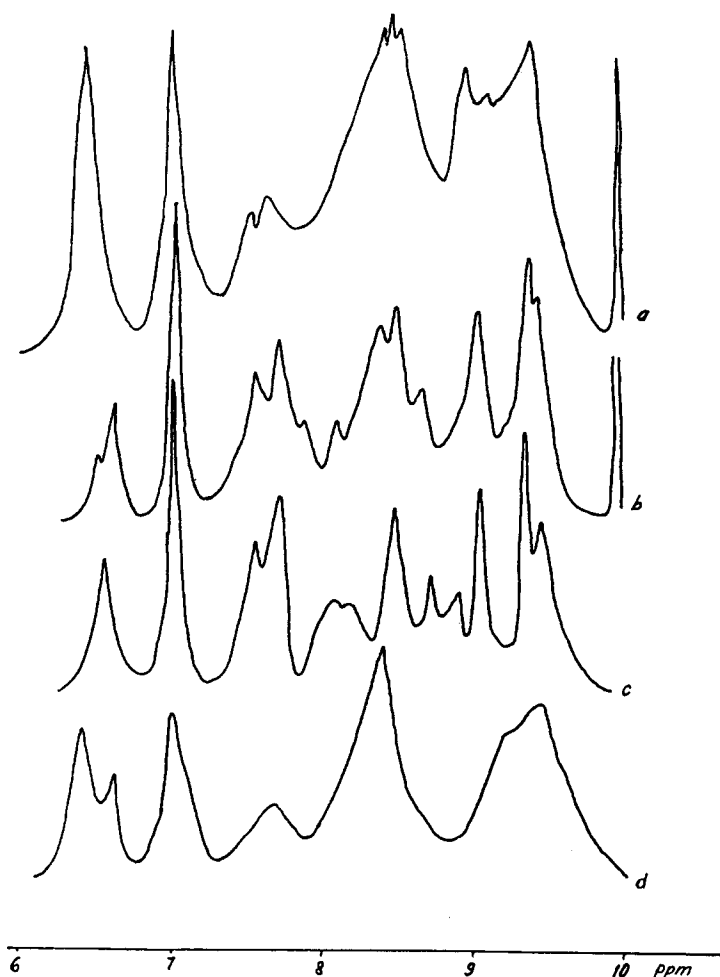| CA	ν, cm^{-1}	$\Delta\nu$, cm^{-1}
—	1725	0
Al(C$_2$H$_5$)Cl	1625	−100
ZnCl$_2$	1612	−113
AlCl$_3$	1580	−145
AlBr$_3$	1590	−135

Fig. 8. NMR spectra of the (1:1) MMA–St copolymer prepared by polymerization in presence of: (a) $ZnCl_2$ at $[ZnCl_2]/[MMA] = 0.6$; (b) $Al(C_2H_5)_2Cl$ at $[Al(C_2H_5)_2Cl]/[MMA] = 0.7$; (c) $Al(C_2H_5)_{1.5}Cl_{1.5}$; and (d) conventional radical copolymer. The spectra have been recorded in 15% solution in o-dichlorobenzene at 150°C with octamethyl-cyclotetrasiloxane as a reference (9.95 ppm).

The apparent copolymerization reactivity ratios in the system MMA–2,6-DCSt–$ZnCl_2$ (see Fig. 7 and Table IV) are varied in a way similar to that in the system MMA–VDC–$ZnCl_2$ (r_1 increase and approaches a limiting value, r_2 decreases) but the change in r_1 is much less than in the MMA–VDC system.   When $AlCl_3$ is used instead of $ZnCl_2$, r_1 and r_2 are changed in a way similar to that in the system MMA–St–$ZnCl_2$ (both are decreased to limiting values at CA content lower than stoichiometric).

As far as different CA's act in different ways in the copolymerization, it is of interest to compare their ability to form complexes with MMA.
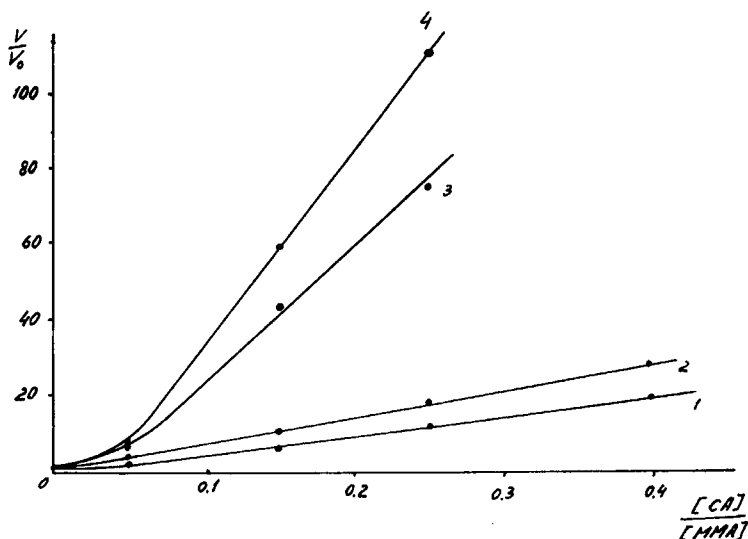
Fig. 9. Dependence of the relative copolymerization rate in the system MMA–St on the ratio [CA]/[MMA]: (1) [MMA]:[St] = 19; (2) [MMA]:[St] = 9; (3) [MMA]: [St] = 0.55; (4) [MMA]:[St] = 0.43. [AIBN] = 5 × 10⁻³ mole/l., t = 50°C, CA = ZnCl₂.

The measure of the relative strength of the complex is the shift of the C=O valent frequency.²² The data are shown in Table V. The data show that all the complexes are stable enough. The complexing and polarizing power of $ZnCl_2$ and $Al(C_2H_5)Cl$ are somewhat lower than those of $AlCl_3$ and $AlBr_3$.

Finally it has been shown that $ZnCl_2$ does not affect the rates of photo-induced homopolymerization of two representative monomers in the second group such as VDC and St, dissolved in ethyl acetate–$ZnCl_2$ (1:0.4) complex as compared to polymerization in pure ethyl acetate.

DISCUSSION

Before discussing the results on copolymerization in presence of different CA's, let us first briefly consider the effects of these compounds in radical homopolymerization of MMA, a monomer in which the functional group forms a complex with the CA's. These effects have to be of primary importance for understanding the copolymerization behavior, because, as shown above, the polymerization rates of the comonomers not forming complexes with the modifiers (and thus the activity of the monomers and of the radicals) remain unchanged in presence of these compounds.

It is known that introduction of relatively small amounts of $ZnCl_2$ and $AlBr_3$[6,19] ([CA]/[MMA] ≃ 0.2) causes considerable increase of propagation rate constant, but the termination constant remains practically unchanged. At higher molar content of $AlBr_3$ the termination constant decreases

sharply and k_p passes through a maximum.   As we had shown earlier,[8–10,23] ESR spectra of PMMA radicals complexed with some of the metal halides differ from those of ordinary PMMA radicals. The difference is attributed to contact interaction of the impaired electron with the metal atom in the CA molecule. In other words there is certain density of the odd electron on the metal atom. On the basis of this, the propagation mechanism involving a CA molecule has been proposed:

$$\text{Rc} + \text{M} \searrow \qquad \text{R} + \text{Mc} \nearrow$$

I

(1)
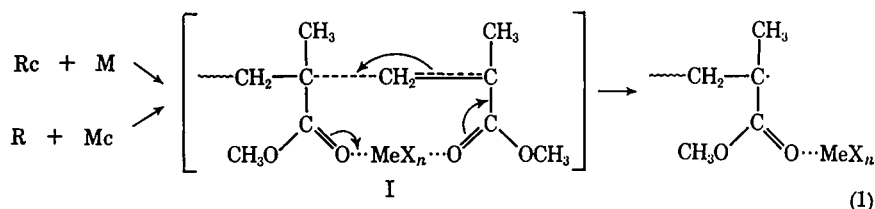
According to the mechanism, the monomer addition occurs by electron transfer through the metal atom in the cyclic transition complex. The efficiency of the process is higher than of ordinary homolytic opening of the double bond. The decrease of k_p at $[\text{AlBr}_3]/[\text{MMA}] > 0.4$ that has been interpreted assuming that, when the monomer and the radical both bound to the CA, the transition state I is not realized or probably requires dissociation of one of the coordination bonds with the modifier (with monomer or with the radical).

This scheme can readily account for the results on copolymerization of MMA with MA or BA (monomers with ideal radical reactivity lower than that of MMA, but forming similar complexes with the modifiers). If the propagation occurs as shown on the scheme, the differences in the relative activities of the double bonds may disappear, and thus the copolymer composition becomes equal to the composition of the monomeric mixture, and apparent values of r_1 and r_2 approach unity.

In the copolymerization of MMA (M_1) with monomers which are not complexed with the modifiers one may expect that variation in values of r_1 is determined on the one hand by the effect of CA on k_{11}, which is independent of the nature of the second monomer, and on the other hand by the effect of CA on the reactivity of the complexed PMMA radical towards the second monomer, which does depend on the nature of the second monomer. The character of r_2 variation depends on the effect of CA on the activity of MMA in the addition to the radical of the second monomer.

The increase of r_1 in the systems MMA–VDC–ZnCl$_2$ corresponds to an increase in k_{11} in the presence of ZnCl$_2$.[6,26]   From the approach of r_1 to constant value at $[\text{ZnCl}_2]/[\text{MMA}] \simeq 0.25$, it may be concluded that further increase of ZnCl$_2$ (and thus of complexed MMA) concentration does not considerably effect the k_{11} value (in accord with the data of Ref. 26).   The same type of behavior is observed in the presence of Al(C$_2$H$_5$)$_2$Cl.   In the system MMA–VDC–AlCl$_3$(AlBr$_3$), the r_1 value passes through maximum with increase of $[\text{AlX}_3]/[\text{MMA}]$.   This behavior correlates quite well with

character of variation of k_p in the system MMA–AlBr$_3$[19] and with the character of variation of the copolymerization rate in system (see Fig. 4) with AlCl$_3$ content.

Now by using the values of r_1 (our data) and literature values[6,26] of k_p at given CA content it is possible to estimate semiquantitatively the effects of CA on the reactivity of PMMA radicals to VDC. At [ZnCl$_2$]/[MMA] $= 0.16$ $r_1 \simeq 13$ ($r_1{}^0 = 2.5$), $r_1/r_1{}^0 = 5.2$ and $k_{11}/k_{11}{}^0 = 2.4$; thus $k_{12}/k_{12}{}^0 \simeq 0.5$ (where superscript zero refers to the system without CA). Though these data correspond to the intermediate content of the CA where free and complexed PMMA radicals are present and therefore cannot be directly used for separate description of the reactivity of the complexed radical, one can see that the reactivity of the complexed PMMA radical of VDC is lower than that of the free radical. In the system MMA–VDC–AlBr$_3$ r_1 has not been determined, but as can be seen from Figure 2 the character of variation of r_1 with [CA]/[MMA] has to be quite similar to that in the system MMA–VDC–AlCl$_3$, where r_1 increases only slightly with increasing [AlCl$_3$]/[MMA] (in the range [AlCl$_3$]/[MMA] ≤ 0.2). As far as $k_{11}/k_{11}{}^0$ $\simeq 3$ at [AlBr$_3$]/[MMA] $= 0.2$, this means that $k_{12}/k_{12}{}^0 > 1$; thus the reactivity of the PMMA radical complexed with AlX$_3$ to VDC molecule is higher than that of free PMMA radical. The different effects of ZnCl$_2$ and AlX$_3$ on the reactivity of PMMA radical can be understood, if one takes into account that complexation brings about higher delocalization of the impaired electron (including the metal atom) and thus decreases its ideal radical reactivity. At the same time, the radical attains some cationic character that may enhance its reactivity to the other monomer due to polar effects. The limit resonance structures are represented by the scheme (2):


$$\text{---CH}_2\text{---C}\cdot \quad \rightleftarrows \quad \text{---CH}_2\text{---C}+ \qquad (2)$$

II
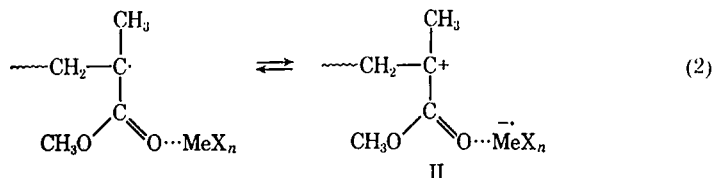
In the case of MMA–ZnCl$_2$–VDC system, the polar effects apparently do not play an important role, but in the case of the stronger polarizing agents AlCl$_3$ and AlBr$_3$ (see Table V) they probably become predominant in the reactivity of the complexed PMMA radical to VDC. The proposed mechanism is further corroborated by the results on the copolymerization with 2,6-DCSt and St. Introduction of ZnCl$_2$ brings about an increase of r_1 at copolymerization with 2,6-DCSt ($e \simeq 0.1$) through at [ZnCl$_2$]/[MMA] $= 0.16$, $r_1/r_0 = 1.7$ and $k_{12}/k_{12}{}^0 = 1.4$. In copolymerization with St ($e = -0.8$), r_1 is already decreased; $r_1/r_0 = 0.4$, at [ZnCl$_2$]/[MMA] $= 0.16$, $k_{12}/k_{12}{}^0 = 7$. Therefore though k_{11} is varied in a similar way in all the systems, the variation in k_{12} changes from a decrease to (VDC) to a progressive increase as the e value of the comonomer becomes more negative.

Introduction of $AlCl_3$ brings about a decrease of r_1 even in copolymerization with 2,6-DCSt. The decrease of r_1 corresponds to increasing importance of ionic structures in the transition state for addition of the second monomer to the complexed PMMA radical.

In the presence of all CA's the values of r_2 decrease with CA concentration. This means that activity of complexed MMA increases as compared to that of pure MMA. The MMA activation in reaction with the radical of the second monomer may be attributed to higher conjugation in the monomer complex (the band for the $\pi \rightarrow \pi^*$ transition in the ultraviolet spectra is shifted to the longer waves by about 700 cm^{-1} [24] and to the polar effect (because complex formation causes subsidiary negative polarization of the electron density in the monomer).

The other and perhaps most important reason of appearance of the marked tendency to alternation in copolymerization (e.g., with styrene) in presence of CA's probably lies in supplemental stabilization of the radical formed after addition of the second monomer to the complexed PMMA radical. It can be described by the structures, one which contains a five-membered oxonium ring (III).
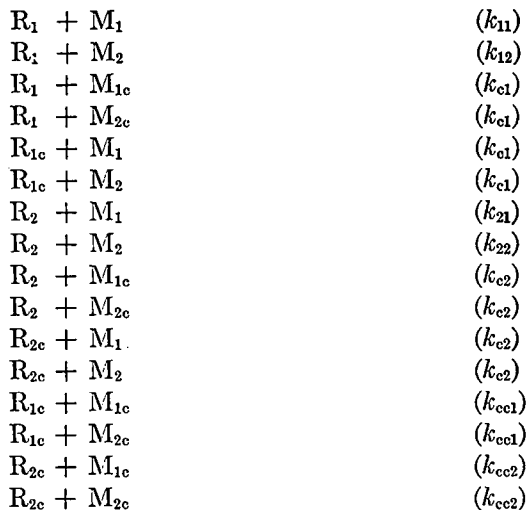

$$(3)$$
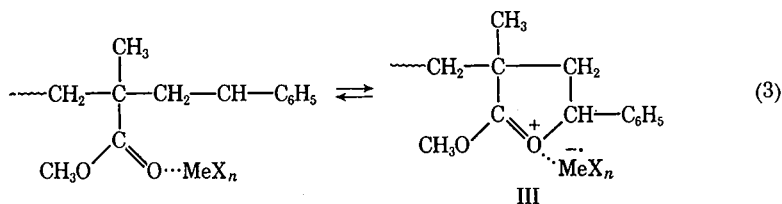
Formation of the ring facilitates addition of one styrene molecule. Addition of the next styrene molecules would however break the supplemental stabilization, because in this case a seven-membered oxonium cycle has to be formed.

A similar mechanism is probably operating in alternating copolymerization of methyl acrylate, acrylonitrile, and MMA with α-olefins in presence of alkylaluminum halides.[11] The presence of CA in these systems provides not only alternating effect but permits preparation of high molecular weight products. In absence of CA, radical polymerization and copolymerization of α-olefins is practically impossible due to degradative chain transfer to the α-olefin. Stabilized radicals like II and III are probably less active in abstraction of hydrogen atoms from α-olefins. Finally, the inability to form unstrained oxonium cycles due to sterical hindrance may be the reason for lack of alternation tendency in copolymerization of vinylpyridines with styrene in presence of zinc salts,[25] though polarizing and resonance effects of zinc salts on the vinylpyridine monomer and radical are quite high (especially in 4- and 2-vinylpyridines).[24,25]

Now let us consider the kinetic scheme describing radical copolymerization in presence of the complexing agents (modificators).

Case I. Both Monomers Form Similar Complexes with the Modifiers

At the copolymerization in such system, 16 elementary reactions have to be taken into account:

$$R_1 + M_1 \qquad\qquad (k_{11})$$
$$R_1 + M_2 \qquad\qquad (k_{12})$$
$$R_1 + M_{1c} \qquad\qquad (k_{c1})$$
$$R_1 + M_{2c} \qquad\qquad (k_{c1})$$
$$R_{1c} + M_1 \qquad\qquad (k_{c1})$$
$$R_{1c} + M_2 \qquad\qquad (k_{c1})$$
$$R_2 + M_1 \qquad\qquad (k_{21})$$
$$R_2 + M_2 \qquad\qquad (k_{22})$$
$$R_2 + M_{1c} \qquad\qquad (k_{c2})$$
$$R_2 + M_{2c} \qquad\qquad (k_{c2})$$
$$R_{2c} + M_1 \qquad\qquad (k_{c2})$$
$$R_{2c} + M_2 \qquad\qquad (k_{c2})$$
$$R_{1c} + M_{1c} \qquad\qquad (k_{cc1})$$
$$R_{1c} + M_{2c} \qquad\qquad (k_{cc1})$$
$$R_{2c} + M_{1c} \qquad\qquad (k_{cc2})$$
$$R_{2c} + M_{2c} \qquad\qquad (k_{cc2})$$

where M_1, M_2, M_{1c}, and M_{2c} are free and complexed monomers and R_1, R_2, R_{1c}, and R_{2c} are free and complexed radicals of the first and the second monomers. It has been assumed that the rate constants k_{c1}, k_{c2} k_{cc1}, k_{cc2} are equal to each other for sets of interactions because for these pairs the copolymer composition approaches the composition of the monomeric mixture at CA content lower than stoichiometric ($[CA]/[M_1]$ + $[M_2]$ $\leq$ 0.2–0.3) where most of the propagation acts occurring can be expressed by a single reaction. On defining

$$\alpha = [R_c]/[R_0]$$

$$\beta = [M_c]/[M_0]$$

where $[R_0]$, $[M_0]$ are total concentrations of radical and monomer, respectively, one can express

$$[R_c] = \alpha[R_0]$$

$$[R] = (1 - \alpha)[R_0]$$

$$[M_c] = \beta[M_0]$$

$$[M] = (1 - \beta)[M_0]$$

The rates of consumption of the monomers M_1 and M_2 are given by eqs. (4) and (5):

$$-d[M_{10}]/dt = k_{11}[R_1][M_1] + k_{c1}[R_1][M_{1c}] + k_{c1}[R_{1c}][M_1] + k_{21}[R_2][M_1]$$

$$+ k_{c2}[R_2][M_{1c}] + k_{cc1}[R_{1c}][M_{13}] + k_{cc2}[R_{2c}][M_{1c}] + k_{c2}[R_{2c}][M_1]$$

$$= [M_{01}]\{[R_{01}][k_{11}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta + k_{c1}\alpha(1 - \beta)$$

$$+ k_{cc1}\alpha\beta] + [R_{02}][k_{21}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta)$$

$$+ k_{cc2}\alpha\beta]\} \quad (4)$$

$$-d[M_{20}] = k_{12}[R_1[M_2] + k_{c1}[R_1][M_{2c}] + k_{c1}[R_{1c}][M_2] + k_{22}[R_2][M_2]$$

$$+ k_{c2}[R_2][M_{2c}] + k_{c2}[R_{2c}][M_2] + k_{cc1}[R_{1c}][M_{2c}] + k_{cc2}[R_{2c}][M_{2c}]$$

$$= [M_{02}]\{[R_{02}][k_{22}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta)$$

$$+ k_{cc2}\alpha\beta] + [R_{01}][k_{12}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta$$

$$+ k_{c1}\alpha(1 - \beta) + k_{cc1}\alpha\beta]\} \quad (5)$$

Diving eqs. (4) by eq. (5) we obtain eq. (6):

$$d[M_{01}]/[d[M_{02}] = ([M_{01}]/[M_{02}]\{[R_{01}][k_{11}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta$$

$$+ k_{cc1}\alpha\beta] + [R_{02}][k_{21}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta)$$

$$+ k_{cc2}\alpha\beta]\}/\{[R_{02}][k_{22}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta$$

$$+ k_{c2}\alpha(1 - \beta) + k_{cc2}\alpha\beta] + [R_{01}][k_{12}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta$$

$$+ k_{c1}\alpha(1 - \beta) + k_{cc1}\alpha\beta]\} \quad (6)$$

In the stationary state,

$$d[R_{01}]/dt = k_{21}[R_2][M_1] + k_{c2}[R_2][M_{1c}] + k_{c2}[R_{2c}][M_1] + k_{cc2}[R_{2c}][M_{1c}]$$

$$- k_{12}[R_1][M_2] - k_{c1}[R_1][M_{2c}] - k_{c1}[R_{1c}][M_2] - k_{cc1}[R_{1c}][M_{2c}] \quad (7)$$

Thus

$$[R_{02}] =$$

$$\frac{[R_{01}][M_{02}]\{k_{12}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta + k_{c1}\alpha(1 - \beta) + k_{cc1}\alpha\beta]\}}{[M_{01}]\{k_{21}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta) + k_{cc2}\alpha\beta\}}$$

$$(8)$$

After substitution of eq. (8) into eq. (6), we obtain:

$$\frac{d[M_{10}]}{d[M_{20}]} = \frac{[M_{10}]}{[M_{20}]} \frac{r_1^{ef}[M_{01}] + [M_{02}]}{r_2^{ef}[M_{02}] + [M_{01}]} \quad (9)$$
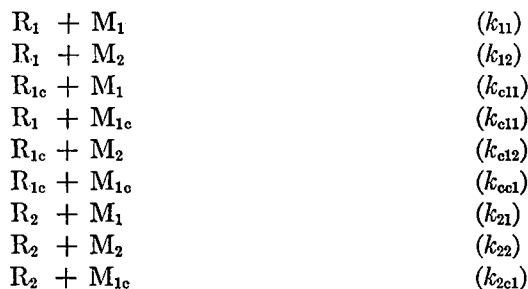
where $r_1^{ef} = \dfrac{k_{11}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta + k_{c1}\alpha(1 - \beta) + k_{cc1}\alpha\beta}{k_{12}(1 - \alpha)(1 - \beta) + k_{c1}(1 - \alpha)\beta + k_{c1}\alpha(1 - \beta) + k_{cc1}\alpha\beta} \quad (9a)$

$r_2^{ef} = \dfrac{k_{22}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta) + k_{cc2}\alpha\beta}{k_{21}(1 - \alpha)(1 - \beta) + k_{c2}(1 - \alpha)\beta + k_{c2}\alpha(1 - \beta) + k_{cc2}\alpha\beta} \quad (9b)$

Equation (9) is analogous in structure to the Mayo–Lewis equation, but r_1^{ef} and r_2^{ef} are functions of the elementary constants and of the values α and β which depend on CA content and on the stability of the complexes formed between the monomers and the radicals with the modifier (CA). As can be easily seen from eqs. (9a) and (9b), regardless of the absolute values of the elementary constants, r_1^{ef} and r_2^{ef} both approach unity with increasing CA content (when α and β approach unity); this has been found in copolymerization of MMA with MA and BA in the presence of $ZnCl_2$ and $AlBr_3$.

Case II.   One of the Monomers (M_1) Forms a Complex with the Modifier

For copolymerization in such systems, 9 types of elementary reactions have to be taken into account:

$$R_1 \;+\; M_1 \qquad\qquad (k_{11})$$
$$R_1 \;+\; M_2 \qquad\qquad (k_{12})$$
$$R_{1c} \;+\; M_1 \qquad\qquad (k_{c11})$$
$$R_1 \;+\; M_{1c} \qquad\qquad (k_{c11})$$
$$R_{1c} \;+\; M_2 \qquad\qquad (k_{c12})$$
$$R_{1c} \;+\; M_{1c} \qquad\qquad (k_{cc1})$$
$$R_2 \;+\; M_1 \qquad\qquad (k_{21})$$
$$R_2 \;+\; M_2 \qquad\qquad (k_{22})$$
$$R_2 \;+\; M_{1c} \qquad\qquad (k_{2c1})$$

The rates of consumption of the monomers M_1 and M_2 in course of the copolymerization are given as:

$$-d[M_{01}]/dt = k_{11}[R_1][M_1] + k_{c11}[R_{1c}][M_1] + k_{c11}[R_1][M_{1c}]$$
$$+ k_{cc1}[R_{1c}][M_{1c}] + k_{21}[R_2][M_1] + k_{2c1}[R_2][M_{1c}]$$
$$= [M_{01}]\{[R_{01}][k_{11}(1-\alpha)(1-\beta) + k_{c11}\alpha(1-\beta) + k_{c11}(1-\alpha)\beta$$
$$+ k_{cc1}\alpha\beta] + [R_2][k_{21}(1-\beta) + k_{2c1}\beta]\} \quad (10)$$

$$-d[M_{02}]/dt = k_{12}[R_1][M_2] + k_{c12}[R_{1c}][M_2] + k_{22}[R_2][M_2]$$
$$= [M_{02}]\{[R_{01}][k_{12}(1-\alpha) + k_{c12}\alpha] + [R_2]k_{22}\} \quad (11)$$

Then by dividing eq. (10) by eq. (11) substituting R_2 through R_{01} from stationary expression for R_{01} one obtains:

$$d[M_{01}]/d[M_2] = ([M_{01}]/[M_2])(r_1^{ef}[M_{01}] + [M_2])/(r_2^{ef}[M_2] + [M_{01}]) \quad (12)$$

where $r_1^{ef} =$

$$\frac{[k_{11}(1-\alpha)(1-\beta) + k_{c11}\alpha(1-\beta) + k_{c11}(1-\alpha)\beta + k_{cc1}\alpha\beta]}{[k_{12}(1-\alpha) + k_{c12}\alpha]} \quad (12a)$$

$$r_2^{ef} = k_{22}/[k_{21}(1-\beta) + k_{2c1}\beta] \quad (12b)$$

Again, the equation for the copolymer composition is analogous in structure to the Mayo–Lewis equation. The parameters r_1^{ef} and r_2^{ef} are variable

functions of the elementary constants and of the values α and β which depend on CA content in the system and on the stability of the complexes formed between the monomer or the radical with the modifier (CA). Equations (12a) and (12b) can qualitatively describe all the observed experimental dependences of r_1^{ef} and r_2^{ef} on CA content (increase or decrease of r_1^{ef} to a limiting value, passing of r_1^{ef} through the maximum; monotonic decrease of r_2^{ef}).

Therefore the results on the copolymerization of MMA with different monomers in presence of some CA's can be expounded by means of a mechanism involving the effect of the modifier on the propagation rate constants with complexed monomers and radicals. The kinetic schemes based on these assumptions (1) exlain why these actually multicomponent systems formally obey at all contents of CA the binary copolymerization equation and (2) could be used for quantitative estimation of reactivity of the complexed monomers and radicals. The latter procedure requires first of all the knowledge of the values of k_p for MMA homopolymerization as a function of CA content, which has not yet been determined in the systems most extensively explored in the paper. Thus we now have been limited only to qualitative analysis of the results. On substituting probable values of kinetic constants into the expressions for r_1 [eqs. (9a) and (12a) and putting $\beta \simeq [CA]/[M_0]$ or $[CA]/[M_1] + (M_2])$ one can infere that the PMMA or PMA radicals form more stable complexes with the modifiers than the monomers. In other words at $[CA]/([MMA] + [MA])$ or $[CA]/[MMA]$ ratios lower than unity, all the propagating radicals are complexed with the modifiers. The conclusion well accounts for the results on copolymerization and is in accord with direct evidence by ESR method.[23]

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