Polymer Bulletin 10, 497-503 (1983)

Polymer Bulletin

Alternating Copolymerization of Ethyl Methacrylate and Butyl Methacrylate with Styrene in the Presence of $ZnCl_2$

Bogdan C. Simionescu, Viorica Talmaciu*, Virgil Bărboiu* and Cristofor I. Simionescu

Department of Organic and Macromolecular Chemistry, Polytechnic Institute of Jassy, 6600 Jassy, Romania
*"P. Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Romania

SUMMARY

The bulk copolymerization of ethyl methacrylate and butyl methacrylate with styrene, at 50°C, in presence of $ZnCl_2$ was investigated. The complexing agent determines the formation of copolymers with high alternating tendency, as proved by the composition of the copolymers and by the distribution of the diads.

INTRODUCTION

Much interest and controversy has been stimulated by alternating copolymerization both in simple monomer mixtures (e.g., maleic anhydride - styrene) and in more complex systems containing an appropriate monomer pair and a Lewis acid. In the last case, the reactions often appear to start spontaneously, even if they are accelerated by the presence of conventional radical initiators, they are relatively insensitive to the presence of chain transfer agents, and the degree of alternating regulation, without reaching 100%, may be very high (1).

The effect of complexing agents in radical copolymerization was mainly studied on methyl methacrylate - styrene system and in this direction one can cite a great number of papers (e.g., 2-5). Copolymerization systems composed of other methacrylates (acrylates) and styrene were practically neglected. To cover this lack, a series of notes will be devoted to the study of alternating radical copolymerization of methacrylates (acrylates) and styrene carried out in presence of $ZnCl_2$. The present paper is dealing with ethyl methacrylate (EtMA) - styrene (St) and butyl methacrylate (BuMA) - St systems.

EXPERIMENTAL

The monomers were purified according to accepted techniques and dried first over anhydrous Na_2SO_4 and then over calcium hydride. $ZnCl_2$ was reagent grade material and was used without further purification.

The copolymerization reactions were performed in bulk, at 50°C, and were initiated by thermal decomposition of azobisisobutyronitrile (0.1% by weight from the monomers). Preparation of the reaction systems was carried out in the dark; the copolymerizations were performed in inert atmosphere and the reactions were stoped at conversions lower than 10%.

The obtained copolymers were separated by pouring the reaction mixture into a mixture of methanol and hydrochloric acid and then reprecipitated twice.

The composition of the copolymers was determined by ^{1}H-NMR spectroscopy, the spectra being registered on a JEOL - C60 HL spectrometer operating at 60 MHz, in $CDCl_3$ solutions, at 50°C.

Copolymerization reactivity ratio values were determined by the Kelen - Tüdős method.

RESULTS AND DISCUSSION

Copolymerization data of the studied systems are given in Tables 1 and 2.

Table 1
Copolymerization data of BuMA (M_1) with St (M_2)

Sample	$[ZnCl_2]/[M_1]$	M_2 in monomer mixture (mole fr.)	M_2 in copolymer (mole fr.)	polym. period (min.)	yield (%)
1	0	0.875	0.82	565	6.31
2	(series I)	0.750	0.70	555	6.02
3		0.625	0.59	500	5.61
4		0.500	0.50	375	4.14
5		0.375	0.42	300	3.79
6		0.250	0.32	240	3.16
7		0.125	0.21	215	3.27
11	0.075	0.875	0.82	305	9.85
12	(series II)	0.750	0.71	225	10.30
13		0.625	0.65	200	9.80
14		0.500	0.57	180	8.79
15		0.375	0.47	150	9.95
16		0.250	0.38	110	10.21
17		0.125	0.26	60	8.04
21	0.200	0.875	0.75	185	7.66
22	(series III)	0.750	0.69	110	9.90
23		0.625	0.62	70	9.01
24		0.500	0.58	60	8.98
25		0.375	0.48	50	8.22
26		0.250	0.40	40	9.06
27		0.125	0.28	25	7.12

The data yielded the following reactivity ratio values:

BuMA (M_1) - St (M_2) system:
$r_1 = 0.66$ $r_2 = 1.00$ $r_1r_2 = 0.66$ ($[ZnCl_2]/[M_1]$) = 0
$r_1 = 0.27$ $r_2 = 0.69$ $r_1r_2 = 0.186$ ($[ZnCl_2]/[M_1]$) = 0.075
$r_1 = 0.02$ $r_2 = 0.56$ $r_1r_2 = 0.011$ ($[ZnCl_2]/[M_1]$) = 0.200

EtMA (M_1) - St (M_2) system:
$r_1 = 0.28$ $r_2 = 1.56$ $r_1r_2 = 0.436$ ($[ZnCl_2]/[M_1]$) = 0
$r_1 = 0.05$ $r_2 = 0.71$ $r_1r_2 = 0.035$ ($[ZnCl_2]/[M_1]$) = 0.100
$r_1 = 0.04$ $r_2 = 0.46$ $r_1r_2 = 0.018$ ($[ZnCl_2]/[M_1]$) = 0.200

For all systems, the Kelen - Tüdős plots are straight lines, so that the simple terminal model of copolymerization can be applied.

Table 2

Copolymerization data of EtMA (M_1) with St (M_2)

Sample	$[ZnCl_2]/[M_1]$	M_2 in monomer mixture (mole fr.)	M_2 in copolymer (mole fr.)	polym. period (min.)	yield (%)
1	0	0.875	0.90	290	6.31
2	(series I)	0.750	0.77	280	3.76
3		0.625	0.75	270	3.50
4		0.500	0.66	260	6.41
5		0.375	0.57	230	2.71
6		0.250	0.45	215	2.56
7		0.125	0.32	190	2.40
11	0.100	0.875	0.85	160	4.36
12	(series II)	0.750	0.75	130	6.26
13		0.625	0.67	110	7.50
14		0.500	0.65	90	7.40
15		0.375	0.59	75	6.25
16		0.250	0.57	60	4.47
17		0.125	0.56	50	3.79
21	0.200	0.875	0.77	70	2.52
22	(series III)	0.750	0.68	45	5.97
23		0.625	0.55	45	8.91
24		0.500	0.55	45	9.10
25		0.375	0.55	40	7.46
26		0.250	0.50	35	6.56
27		0.125	0.44	25	5.46

The dependence of the copolymerization reactivity ratio values and of r_1r_2 products with $[ZnCl_2]/[M_1]$ is presented in Figure 1.

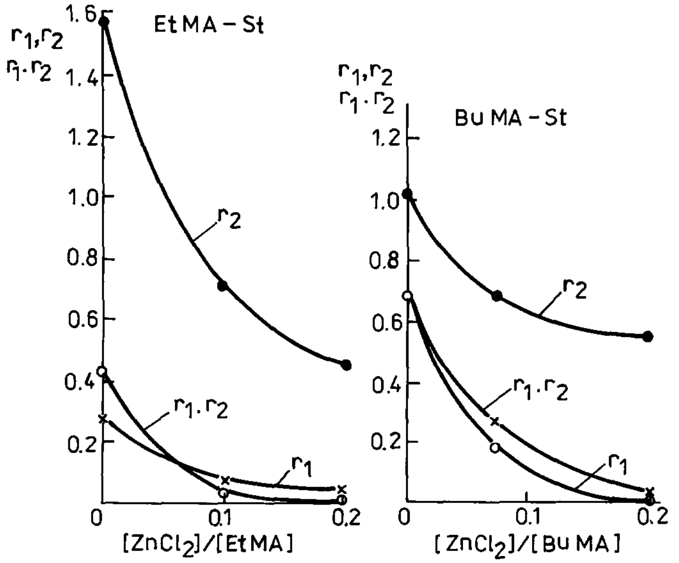

Figure 1. Dependence of r_1, r_2 and r_1r_2 product on $[ZnCl_2]/[M_1]$ ratio for the studied systems.

For both systems, r_1 and r_2 values decrease with increasing $[ZnCl_2]/[M_1]$ ratio and the product r_1r_2 becomes very low. This is usually related to a high alternating tendency of the copolymer.

As known (4), the introduction of relatively small amounts of $ZnCl_2$ in the reaction mixture causes considerably increase of propagation rate constant, while the termination rate constant remains practically unchanged. In this context, Table 3 presents the evolution of copolymer yield with $[ZnCl_2]/[M_1]$ ratio, for a constant copolymerization period and for a 1:1 initial ratio of the two monomers. The copolymer yield markedly increases with the increase of $ZnCl_2$ amount.

Table 3

Variation of copolymer yield with $[ZnCl_2]/[M_1]$ ratio[a]

$[ZnCl_2]/[M_1]$	Copolymer yield (%)	
	BuMA - St	EtMA - St
0	1.69	1.79
0.075	7.29	8.20
0.112	10.98	10.48
0.150	14.01	11.47
0.225	24.86	24.28
0.297		35.14
0.375	72.22	
0.450	86.04	88.17

a - polymerization period, 150 min., $[M_1]/[M_2]$ = 1:1

As expected (6,7) the NMR signal of the protons of the $-CH_2-OCO$ group of the methacrylic units is sensitive to the neighbouring monomer units, being splitted in four components (Figure 2).

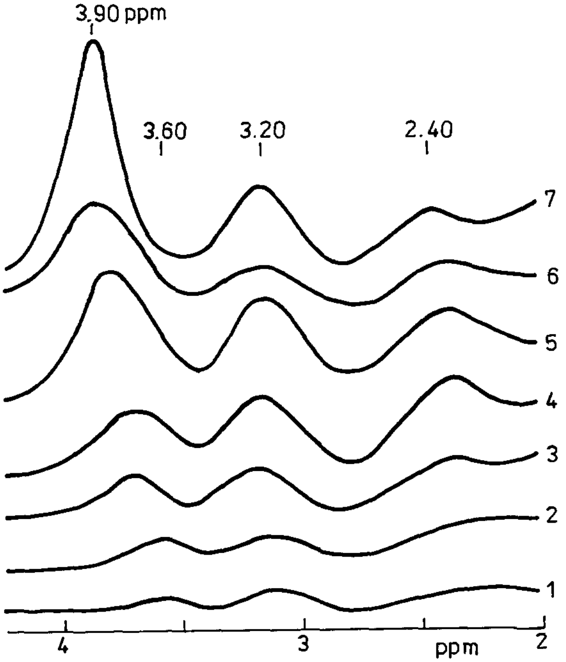

Figure 2.

^1H NMR signals of the $-CH_2-OCO$ group protons in BuMA - St copolymers (series III).

The most probable assignment of these components is the following one: 2.40 ppm for 212 mm triads, 3.20 ppm for 212 mr, 112 mm and 112 rm triads, 3.60 ppm for 212 rr, 112 mr and 112 rr triads, and 3.90 ppm for 111 triads (6,7).

The large errors in apreciation of the intensities of the peaks do not allow the calculation of triad sequences to obtain the coisotacticity parameter. However, the calculation of diads is possible, considering that the 3.90 ppm peak results from 11 type diads while all the other ones result from 12 type diads. According to Harwood and Ritchey (8), one can obtain the following parameters: f_{12} - the fraction of 12 type diads, $\bar{l}_1$ and $\bar{l}_2$ - the average lengths of block sequences composed of M_1 and M_2, and the product r_1r_2, where $r_1 = \bar{l}_1 - 1$ and $r_2 = \bar{l}_2 - 1$. Figure 3 (a,b) presents the variation of these parameters with the initial ratio of the comonomers.

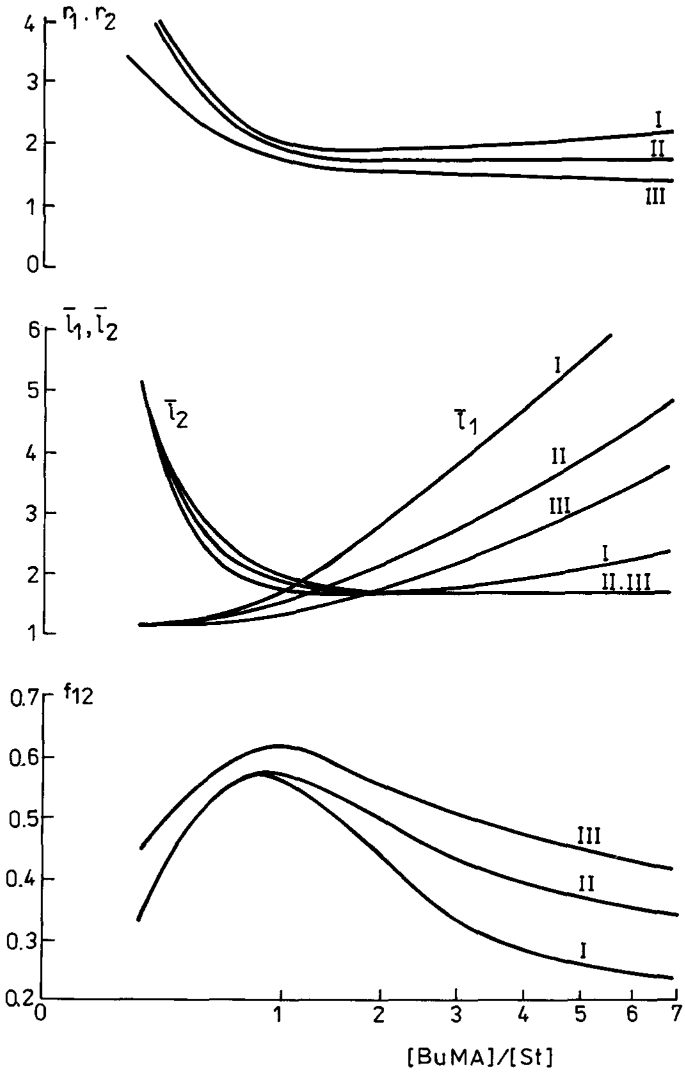

Figure 3 (a). Dependence of f_{12}, $\bar{l}_1$ and $\bar{l}_2$ and r_1r_2 on the initial ratio of the comonomers. Abscissa is given in $\left\{[M_1]/[M_2]\right\}^{1/2}$.

The weight of 12 type diads presents a maximum value situated approximately at a 1:1 ratio of the two comonomers for the system BuMA - St. For the system EtMA - St, the three curves present three different maxima: at an about 3:1 ratio for samples I, at an about 1.5:1 ratio for samples II and at an about 1:1 ratio for samples III. The positions of these maxima correspond to the positions of the minima of r_1r_2 products.

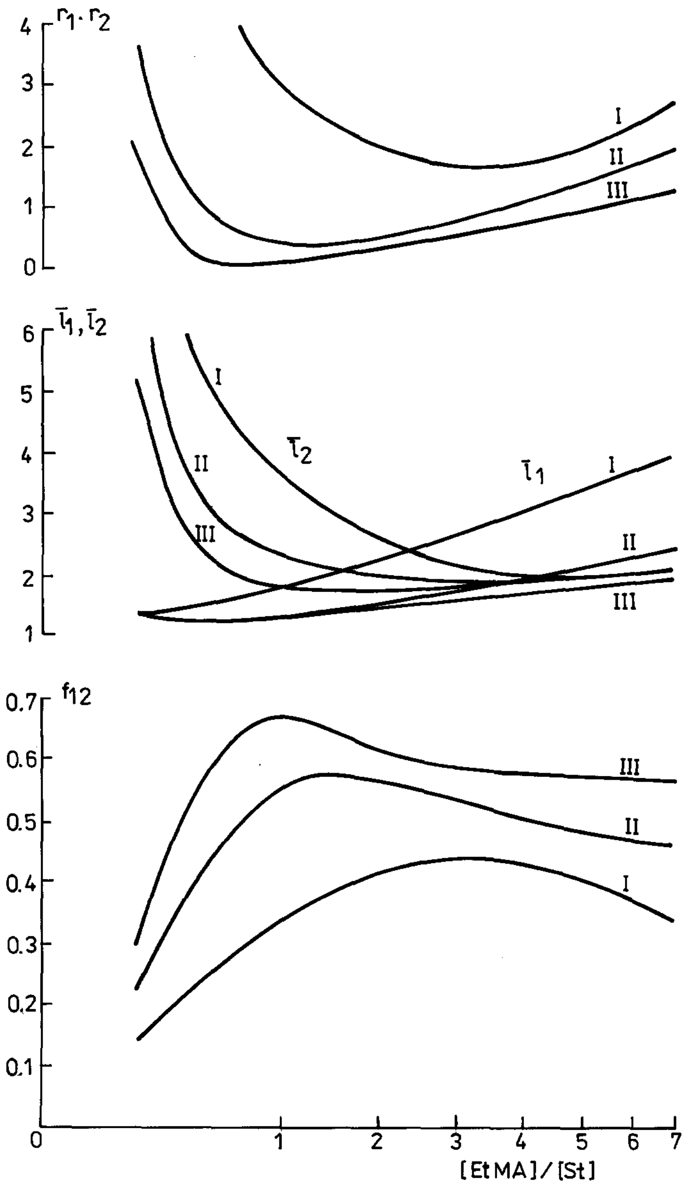

Figure 3 (b).

The amplitudes of the f_{12} maxima are approximately equal in BuMA - St series, but quite different in EtMA - St system. According to these data, one can consider that $ZnCl_2$ influences mainly the copolymerization of EtMA with St.

As concerns the variation of the average lengths of block sequences $\bar{l}_1$ and $\bar{l}_2$, in BuMA - St system the complexing agent influences mainly the BuMA units, while in EtMA - St system it influences both EtMA and St units. The observed differences are due to the values of the reactivity ratios in the initial systems (series I).

All these data confirm that the presence of the complexing agent increases the alternating tendency in the copolymers.

In the present paper, the $[ZnCl_2]/[M_1]$ ratio was considered for the interpretation of experimental data, the methacrylic monomers being the ones forming complexes with $ZnCl_2$. The formation of the complexes was evidenced by measuring the shift of the $>C=O$ band frequency (Table 4).

In Table 4 the shift of the same band of methyl methacrylate (copolymerization system: methyl methacrylate - St in presence of $ZnCl_2$) is also given (ref. 4).

Table 4
Effect of $ZnCl_2$ on >C=O band in the IR spectra of methacrylic monomers

monomer / $ZnCl_2$	>C=O ν(cm^{-1})	$\Delta\nu$(cm^{-1})
BuMA	1718	-
BuMA / $ZnCl_2$	1597	-121
EtMA	1713	-
EtMA / $ZnCl_2$	1595	-118
MMA	1725	-
MMA / $ZnCl_2$	1612	-113

CONCLUSIONS

The bulk copolymerization of BuMA and EtMA with St, in presence of $ZnCl_2$, leads to copolymers having a pronounced alternating tendency, even if relatively small amounts of $ZnCl_2$ are introduced in the reaction mixture. The presence of the complexing agent causes a considerably increase of the rate of polymerization.

The mechanism of copolymerization in presence of $ZnCl_2$ will be discussed in a next paper.

REFERENCES

1. C.H.Bamford and P.J.Malley, J.Polym.Sci., Polym.Lett.Ed. 19, 239 (1981).
2. H.Hirai, T.Tanabe and H.Koinuma, J.Polym.Sci., Polym.Chem. Ed. 18, 203 (1980).
3. H.Hirai and M.Komiyama, J.Polym.Sci., Polym.Lett.Ed. 12, 673 (1974).
4. V.P.Zubov, L.I.Valuev, V.A.Kabanov and V.A.Kargin, J.Polym. Sci. A-1 9, 833 (1971).
5. M.Hirooka, Pure Appl.Chem. 53, 681 (1981).
6. F.A.Bovey, "High Resolution NMR of Macromolecules", Academic Press New York, London (1972).
7. J.Podesva and N.Doskocilova, Makromol.Chem. 178, 2383 (1977).
8. H.J.Harwood and W.M.Ritchey, J.Polym.Sci. B-2, 601 (1964).

Accepted August 24, 1983

C