

**Plasma-Induced Polymerization****2. Bulk Copolymerization of Alpha-Methyl Styrene with Methyl Methacrylate and Acrylonitrile**

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SUMMARY

The plasma-induced bulk copolymerization of alpha-methyl styrene (MS) with methyl methacrylate (MMA) and with acrylonitrile (AN) was studied at room temperature. The reactivity ratio values:

$$\begin{array}{lll} \text{MMA} - \text{MS} & r_{\text{MMA}} = 0.42 & r_{\text{MS}} = 0.22 \\ \text{AN} - \text{MS} & r_{\text{AN}} = 0.03 & r_{\text{MS}} = 0.14 \end{array}$$

as well as the configurational parameter  $\bar{v} = 0.21$  for the first system indicate that both systems can be described by the simple terminal model, neglecting the depolymerization reactions.

INTRODUCTION

In a previous paper (SIMIONESCU et al., 1980) the plasma-induced bulk copolymerization of methyl methacrylate (MMA) and styrene was presented. According to the compositional and configurational data, a radical mechanism of copolymerization was proposed. This paper deals with two copolymerization systems, namely MMA - alpha-methyl styrene (MS) and acrylonitrile (AN) - MS. The literature data (WITTMER, 1967) indicate that during propagation both systems present depolymerization reactions which have to be taken into account especially at elevated temperatures. Considering that plasma-induced copolymerization can be performed at room temperature, one can presume that these copolymerizations could be treated by the simple terminal model, neglecting the depolymerization reactions.

1. METHYL METHACRYLATE - ALPHA-METHYL STYRENE SYSTEM

The copolymerizations were performed in sealed ampoules according to the described procedure (SIMIONESCU et al., 1980). The samples were kept in dark at 22°C during 19 days, then opened and precipitated in methanol. The copolymerization data are presented in Table 1.

TABLE 1  
MMA ( $M_1$ ) - MS ( $M_2$ ) copolymerization data

Sample	Initial mixture $x = [M_1] / [M_2]$	Conversion (%)	Copolymer composition $y = d[M_1] / d[M_2]$	Intrinsic viscosity (ml/g)
1	0.17	traces		
2	0.41	0.06	0.69	30
3	0.73	0.15	0.99	46
4	1.22	0.22	1.36	64
5	2.04	0.32	1.56	92
6	3.67	0.44	2.20	124
7	8.57	0.55	4.44	204

Copolymer compositions were determined by  $^1\text{H-NMR}$  spectroscopy, the spectra being registered in  $\text{CDCl}_3$  solutions at  $60^\circ\text{C}$  on a JEOL - C60 HL spectrometer operating at 60 MHz; intrinsic viscosities were determined in  $\text{CHCl}_3$  at  $26^\circ\text{C}$ .

The copolymerization diagram is presented in figure 1. The Kelen - Tüdös plot (figure 2) gives the reactivity ratio values

$$r_1 = 0.42$$

$$r_2 = 0.22$$

The straight line in figure 2 indicates a terminal model of copolymerization at  $22^\circ\text{C}$ . The results are very close to those obtained by WITTMER (1967) at  $20^\circ\text{C}$  by radical initiation ( $r_1 = 0.50$ ,  $r_2 = 0.25$ ; recalculated using Kelen - Tüdös equation and Wittmer's data:  $r_1 = 0.45$ ,  $r_2 = 0.24$ ).

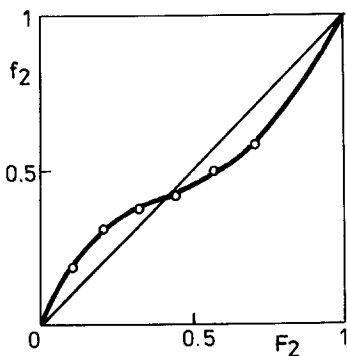


Fig. 1. Copolymerization diagram (MMA - MS).

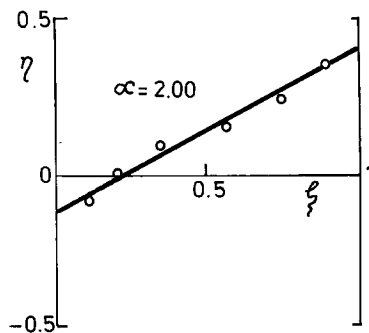


Fig. 2. The Kelen - Tüdös plot (MMA - MS system).

Consequently, these reactivity ratio values and the initial feed ratio ( $x$ ) can be considered for configurational parameter calculation according to ITO et al. (1967) method.

The methoxy signal in  $^1\text{H-NMR}$  spectra is split mainly in two parts: A (3.6 ppm) and B (3.2 ppm) assigned to the methoxy group having no screening influence (A) and screened by only one aromatic nucleus (B). The C part, assigned to a methoxy group screened by two aromatic nuclei, is insignificant as compared with A and B parts.

The ITO et al. (1967) equations are

$$1/(1 - F_A^{1/2}) = (r_1/\bar{\nu})x + 1/\bar{\nu}$$

$$1 + 2F_A/F_B = (r_1/\bar{\nu})x + 1/\bar{\nu}$$

where  $F_A$  and  $F_B$  are, respectively, the A and B fractions of the methoxy signal and  $\bar{\nu}$  is the probability of an alternating coisotactic addition (having the methoxy group and the aromatic ring on the same side of the main chain).

The experimental data give the value  $\bar{\nu} = 0.21$  indicating a rather high cosyndiotactic preference for the alternating addition.

Figure 3 represents the calculated A and B fractions with  $\bar{\nu} = 0.21$  (full line) and the experimental ones, indicating a good agreement between experimental and calculated data. It also clearly points to why the C fraction of the methoxy signal can not be measured in the  $^1\text{H-NMR}$  spectra; the value of this fraction amounts to less than 5% on all the copolymerization domain.

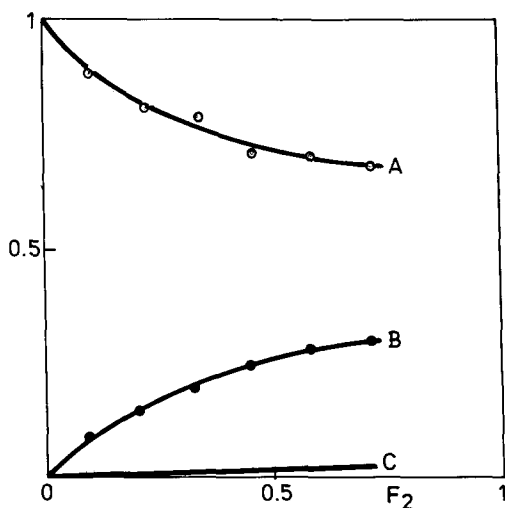


Fig. 3. Methoxy signal fractions (— calculated, •• experimental).

Working between  $60^\circ$  and  $147^\circ$  C, IZU et al. (1972) established the  $\bar{\nu}$ -value dependence on copolymerization

temperature for this system. The value found for 22° C copolymerization temperature agrees with their Arrhenius plot, confirming that the terminal model of copolymerization properly describes the system at 22° C.

## 2. ACRYLONITRILE - ALPHA-METHYL STYRENE SYSTEM

The same experimental procedure was followed for AN - MS mixtures, except the copolymerization time that was 32 days. The samples were precipitated with petroleum ether. The copolymerization results are presented in Table 2.

TABLE 2  
AN (M<sub>1</sub>) - MS (M<sub>2</sub>) copolymerization data

Sample	Initial mixture $x = [M_1] / [M_2]$	Conversion (%)	Copolymer composition $y = d[M_1] / d[M_2]$	Intrinsic viscosity (ml/g)
11	0.28	0.65	0.67	98
12	0.66	0.77	0.82	90
13	1.18	1.32	0.85	128
14	1.97	1.70	0.89	83
15	3.29	0.41	1.04	102
16	5.91	0.50	1.27	114
17	13.79	0.22	1.70	78

Copolymer compositions were determined from the <sup>1</sup>H-NMR spectra registered in CDCl<sub>3</sub> at 60° C and the intrinsic viscosities were measured in CHCl<sub>3</sub> at 25° C. The copolymerization diagram is presented in figure 4. The Kelen - Tüdös plot (figure 5) gives the reactivity ratio values

$$r_1 = 0.03$$

$$r_2 = 0.14$$

At 20° C, WITTMER (1967) obtained  $r_1 = 0.03$  and  $r_2 = 0.11$ ; his data recalculated according to the Kelen - Tüdös equation give  $r_1 = 0.03$ ,  $r_2 = 0.12$ . Both the copolymerization diagram and the Kelen - Tüdös plot confirm the great tendency to alternate of these two comonomers. However, the Kelen - Tüdös plot being a straight line, the system can be described by the simple terminal model of copolymerization.

## CONCLUSIONS

Both copolymerization systems can be described by the simple terminal model of copolymerization, due to the relatively low copolymerization temperature, which permits to neglect the depolymerization reactions. The reactivity ratio values and the configurational

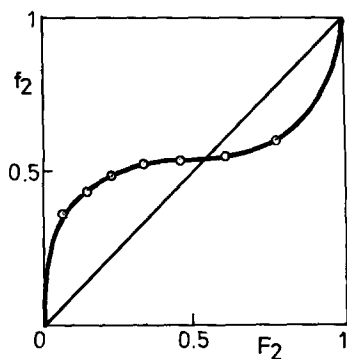


Fig. 4. Copolymerization diagram (AN - MS).

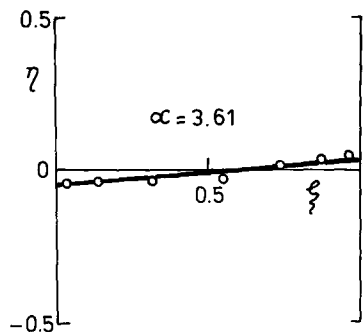


Fig. 5. The Kelen - Tüdös plot (AN - MS system).

parameter (for MMA - MS system) are similar with those obtained by classical radical mechanisms.

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