Polymer Bulletin 2, 809–815 (1980)

Polymer Bulletin

Plasma-Induced Polymerization

1. Bulk Copolymerization of Methyl Methacrylate and Styrene

B. C. Simionescu[1], Almeria Natansohn[2] and C. I. Simionescu[1]

[1]Department of Organic and Macromolecular Chemistry, Polytechnic Institute, 6600 Jassy, Romania
[2]"P. Poni" Institute of Macromolecular Chemistry, 6600 Jassy, Romania

Dedicated to Professor Herman Mark at the occasion of his 85th anniversary

SUMMARY

High molecular weight methyl methacrylate (M_1) - styrene (M_2) copolymers were obtained by plasma-induced bulk copolymerization. The reactivity ratios, determined by Kelen - Tüdös method, were shown to be $r_1=0.41\pm0.01$ $r_2=0.57\pm0.01$ and the coisotactic alternating addition probability $\sigma=0.48\pm0.02$. These data indicate a radical mechanism of copolymerization.

INTRODUCTION

Last years numerous papers dealt with chemical reactions carried out in plasma conditions. As concerns macromolecular chemistry, a great number of polymerizations were performed in low-pressure plasma obtained by radiofrequency discharges (SHEN, 1976). The structure and properties of plasma-obtained polymers considerably differ from those of the conventional ones, these polymers being generally amorphous and highly crosslinked.

Recently, OSADA et al. (1978a, b; 1979) reported the polymerization of methyl methacrylate through plasma initiation. The resulting polymer was shown to have a very high molecular weight and to be relatively monodisperse.

It seems to be interesting to study different polymerization, copolymerization and block copolymerization reactions initiated in this manner. The initiation reaction, taking probably place in the gas phase, can be easely controlled; the molecular weight and polydispersity of the polymers must be directly related to the reaction conditions; and, at the same time, the activity of the propagating species appears to be unusually high and very stable in time even at room temperature.

The present paper deals with the plasma-induced bulk copolymerization of methyl methacrylate (MMA, M_1) and styrene (S, M_2).

0170–0839/80/0002/0809/$01.40

EXPERIMENTAL

The monomers were twice distilled at reduced pressure under nitrogen, dried on CaH_2, redistilled and used immediately after. The comonomer mixtures were introduced in Pyrex ampoules, frozen in liquid nitrogen after degassing, evacuated to 10^{-3}-10^{-4} Torr and sealed. The electrical discharge was operated between two electrodes situated at 4.0 and 6.5 cm from the comonomers sample, coupled to a high-frequency discharge generator (frequency - 2.5 MHz, power - 100 W). The discharge was generated during 60 seconds. The samples were kept in dark, at room temperature, during eleven days, and then opened, diluted with benzene and precipitated with methanol.
NMR spectra were registered in $CDCl_3$ solutions at 60°C on a JEOL C-60HL spectrometer operating at 60 MHz.

RESULTS AND DISCUSSION

In order to determine the reactivity ratio values, the copolymerization data were processed using the KELEN and TÜDÖS (1975) method. The initial monomer mixtures and the copolymer compositions determined by NMR are given in Table 1.

TABLE 1
Copolymerization data

Sample	Initial mixture $x=[M_1]/[M_2]$	Conversion (%)	Copolymer composition $y=d[M_1]/d[M_2]$	Intrinsic viscosity^x (ml/g)
1	0.154	0.78	0.21	405
2	0.361	0.82	0.50	395
3	0.650	1.10	0.70	462
4	1.084	1.18	1.01	511
5	1.808	1.30	1.24	453
6	3.255	1.40	1.95	505
7	7.612	2.53	3.71	570

^{x}-determined in benzene at 25°C

The Kelen - Tüdös plot is represented in figure 1. The obtained reactivity ratio values are

$$r_1 = 0.41 \pm 0.01$$
$$r_2 = 0.57 \pm 0.01$$

Their confidence interval for 95% probability level was determined to be $\Delta r_1 = 0.009$ and $\Delta r_2 = 0.011$ by the method proposed by KELEN et al. (1980). The reliability of the chosen data was tested by a relation found by TÜDÖS and KELEN. These values are of the same order of magnitude with those published for radical bulk copolymerizations of MMA and S at higher temperatures (BRANDRUP and IMMERGUT, 1975).
From the ^1H-NMR spectra of these copolymers it is

possible to determine the probability of coisotactic alternating addition, σ, using the fractions of the three parts of the methoxy signal. Its splitting is due to the aromatic screening effect given by the adjacent benzene rings. A typical NMR spectrum of the methoxy group is given in figure 2.

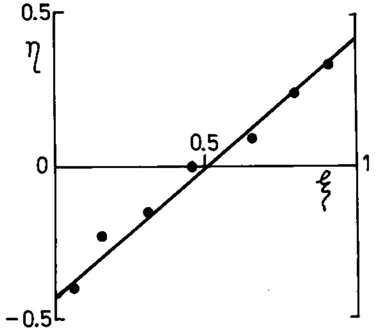

Fig. 1. The Kelen - Tüdős plot (α= 1.33).

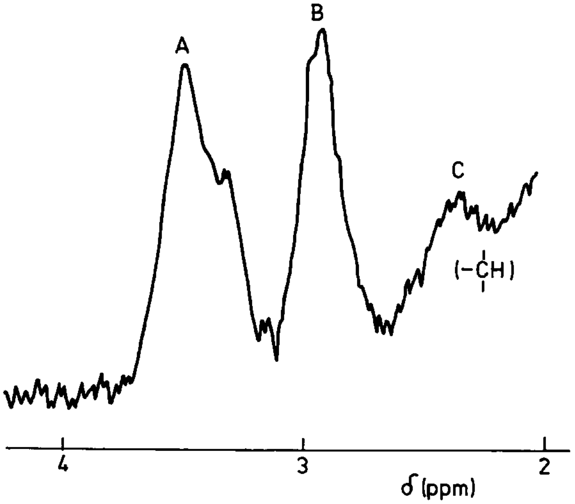

Fig. 2. Methoxy group signal (sample 4).

The fractions of the A and B parts of the methoxy signal were determined from the spectra integrals and the C part was determined by difference, due to the overlapping of the $-\overset{|}{\underset{|}{C}}H$ signal from the main chain.

In order to obtain the σ-values, M_1-centered triad fractions were calculated according to HARWOOD and RITCHEY (1964).

The method proposed by HARWOOD et al. (1969) is based on the equations

$$(F_A - f_{111})/f_{212} = (1 - \sigma)f_{112}/f_{212} + (1 - \sigma)^2$$
$$F_B/f_{212} = \sigma f_{112}/f_{212} + 2\sigma(1 - \sigma) \qquad (1)$$
$$F_C/f_{212} = \sigma^2$$

where F_A,.. is the fraction of the A,.. part of the methoxy signal and f_i.. is the fraction of the i.. triad.
Their plots are represented in figure 3.

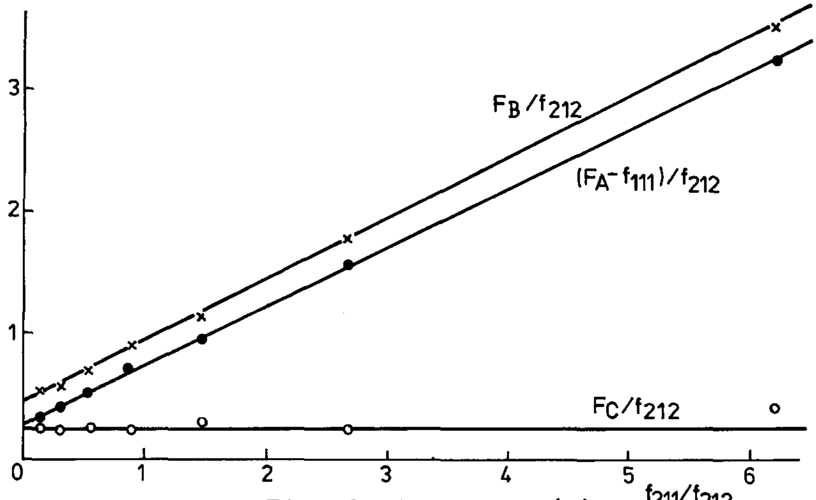

Fig. 3. Equations (1).

The ITO et al. (1967) equations are represented in figure 4. These equations are

$$1/(1 - F_A^{1/2}) = (r_1/\sigma)x + 1/\sigma \qquad (2)$$
$$1 + 2F_A/F_B = (r_1/\sigma)x + 1/\sigma$$

The SAN ROMAN et al. (1979) relation

$$1 - F_A^{1/2} = \sigma P_{12} \qquad (3)$$

where P_{12} is the probability of M_2 addition at a M1-ended macroradical, is represented in figure 5.
The average σ-value is

$$\sigma = 0.48 \pm 0.02$$

In order to verify this value, figure 6 represents the calculated and found signal fractions.
The experimental results are shown to be in good agreement with those calculated for $\sigma = 0.48$.
As well as for the reactivity ratio values, the σ-value is in the range of those previously found for radical copolymerization of MMA and S: $\sigma = 0.48$ (ITO and

YAMASHITA, 1965; ITO et al., 1967); σ= 0.50 (STROGANOV et al., 1974; KATRITZKY et al., 1974); σ= 0.46 (SAN ROMAN et al., 1979).

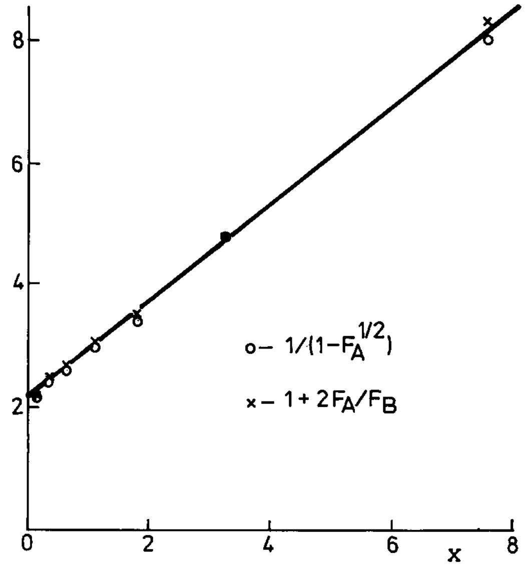

Fig. 4. Equations (2).

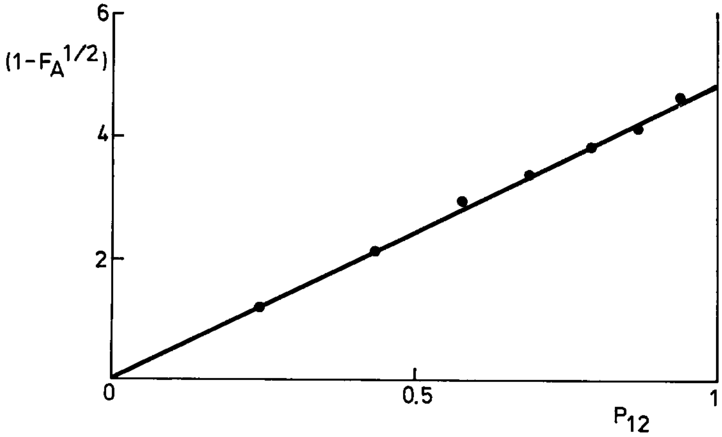

Fig. 5. Equation (3)

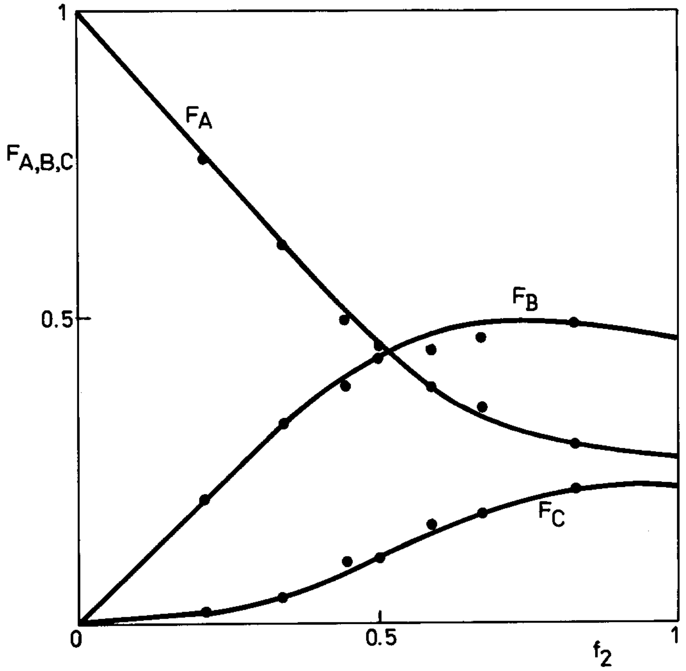

Fig. 6. Methoxy signal fractions (—— calculated, •••• experimental).

From these preliminary results on plasma-induced polymerization, a radical mechanism could be considered, due to the similarity of compositional and configurational data of the plasma-induced copolymers with those obtained by classical radical copolymerizations. As concerns the copolymer molecular weights, intrinsic viscosity data, presented in Table 1, prove that very high molecular weight copolymers are obtained.

CONCLUSIONS

Plasma-induced copolymerization of MMA and S led to very high molecular weight polymers with compositions and configurations very close to those obtained by radical mechanisms. Considering in addition that the presence of small amounts of radical inhibitors impedes the progress of the reaction, one can presume that the plasma-induced process is also a radical one.

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Received June 18 / Accepted June 21,198o