

## **Effect of an Inert Solvent on the Copolymerization of Styrene/Diethylmaleate**

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*Dedicated to Prof. C.I. Simionescu on the occasion of the 60th anniversary of his birthday*

### ABSTRACT

We studied the effect of an inert solvent (benzene) on the overall rate of copolymerization in the system styrene/diethylmaleate (ST/DEM), initiated with azo-bis-iso-butyro-nitrile (AIBN) at 50°C. The experimental results can be interpreted on the hot radical theory.

### INTRODUCTION

There are many problems not sufficiently clarified in the field of copolymerization kinetics. One of these is the effect of the reaction medium on the overall rate of the process. A lot of investigations show that the composition and rate can not be described within the scope of classical copolymerization theory [1-5]. The role of inert solvent was first explained by Tüdös [6] on the basis of the hot radical theory for homopolymerization reactions. This theory has recently been extended to the general case of binary copolymerization, in which both monomers are able to homopolymerize [7]. It is also interesting to examine the effect of the reaction medium in the special case when one of the monomers applied is not capable to homopolymerize. This condition leads namely, to some simplifications in the kinetic treatment.

### EXPERIMENTAL

Styrene/diethylmaleate ( $St=m_1$  and  $DEM=m_2$ ) model system was copolymerized in the presence of AIBN initiator and benzene (Bz), at 50°C. Conversion ( $p\%$ ) and the overall rate of copolymerization ( $W_2$ ) were followed dilatometrically. Copolymer composition was determined by micro-analysis of the oxygen-content [8]. The rate of initiation ( $W_1$ ) was determined by inhibition method [9].

## RESULTS AND DISCUSSION

The conversion-time relationships are illustrated in Fig.1.

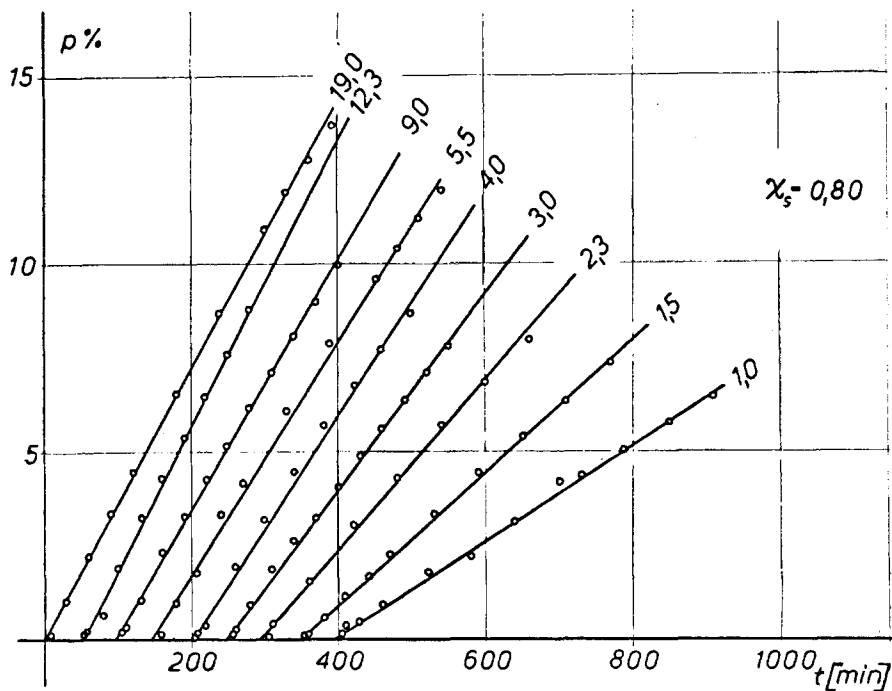


Figure 1. Conversion vs. time curves at different value of  $m_1/\overline{m}_2$  (noted at each curve). The molar function of benzene;  $\chi_s = 0,80$ .

$W_2$  values were determined from the slopes of the corresponding straight lines. The lines characterized by a parameter denoting the initial molar ratios of St/DEM ( $=m_1/m_2$ ) and are shifted on the time scale. According to the classical rate equation [10] in the case of constant monomer composition ( $m_1/m_2 = \text{const}$ ), the value of  $W_2/\sqrt{\overline{W}_2}m_1$  - which is analogous to the overall rate constant of polymerization - is to be independent of dilution. The experimental data (see also Fig.2) show, however, a very significant dilution-effect.

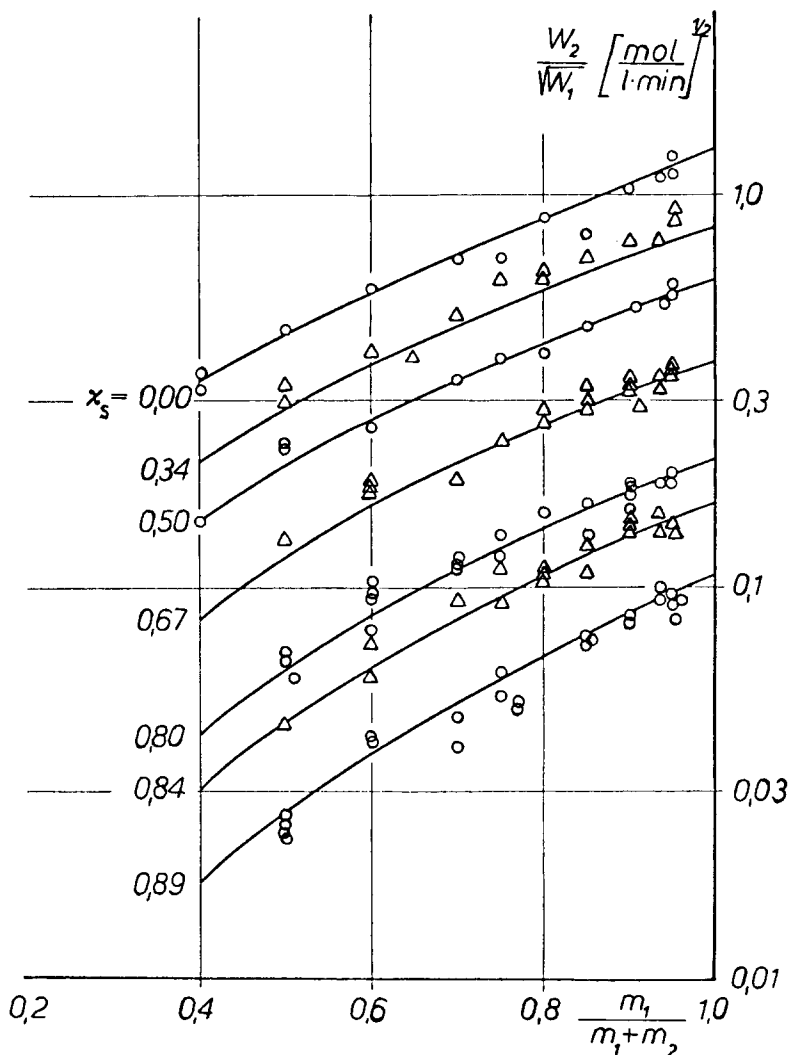


Figure 2. The  $W_2/\sqrt{W_1}$  values as a function of the molar fraction of styrene at different dilution ( $\chi_s$  value noted at each curve).

In considering these results, we tried to interpret the copolymerization of the St/DEM/Bz system in terms of the hot radical theory [7]. In the system studied only six chain propagation steps were taken into account, i.e., neither hot, nor cold radicals of DEM are capable to react with DEM ( $\rho_2 = \rho_1^* = 0$ ). According to the principles outlined in [7] the full description of the copolymerization of the St/DEM/Bz system requires 11 parameters as follows:

$$\rho_1 = \frac{k_{11}}{k_{12}}, \quad \rho_1^* = \frac{k_{11}}{k_{12}}, \quad \delta_1 = \frac{\sqrt{k_{4,1}}}{k_{11}} \quad (1-3)$$

$$\gamma_1 = \frac{k_{7,1}}{k_{11}}, \quad \gamma_{11} = \frac{k_{7,11}}{k_{11}^*}, \quad \gamma_{12} = \frac{k_{7,12}}{k_{11}^*} \quad (4-6)$$

$$\underline{\gamma}_2 = \frac{k_{7,2}}{k_{21}^*}, \quad \underline{\gamma}_{21} = \frac{k_{7,21}}{k_{21}^*}, \quad \underline{\gamma}_{22} = \frac{k_{7,22}}{k_{21}^*} \quad (7-9)$$

$$\underline{\delta}_2 = \frac{\sqrt{k_{4,2}}}{k_{21}} \quad \text{and} \quad \phi = \frac{k_{4,12}}{(k_{4,1}k_{4,2})^{1/2}} \quad (10-11)$$

From this parameter set the reactivity ratios were determined directly from composition data and found to be approximately independent of dilution. [ $\rho_1 = \rho_1^* = 6.59$ ]. The reactivity ratio is in good agreement with that of Lewis and Mayo [11]. Since in the present system  $k_{22} = k_{22}^* = 0$  the underlined deactivation constants and  $\underline{\delta}_2'$  had to be defined differently from the corresponding quantities in [7].

It should be noted that  $\delta_1$ ,  $\gamma_1$  and  $\gamma_{11}$  are experimental data characteristic of the homopolymerization of styrene [6] and so these values are known from independent experiments. On the other hand, in numeric calculations the  $\underline{\gamma}_2'$ ,  $\underline{\gamma}_{21}'$  and  $\underline{\gamma}_{22}'$  cannot be separated from the values  $\phi$  and  $\underline{\delta}_2'$ .

Taking into account the above parameters we may derive the following deactivation functions:

$$D_1 = \frac{m_1 + m_2/\rho_1}{\gamma_{11}m_1 + \gamma_{12}m_2 + \gamma_1s} \quad \text{and} \quad D_2' = \frac{m_1}{\gamma_{21}'m_1 + \gamma_{22}'m_2 + \gamma_2's} \quad (12,13)$$

and with the aid of these, the effective "constants" of the classical treatment can be written as follows:

$$\tilde{\rho}_1 = \frac{1 + D_1}{1 + \frac{\rho_1}{\rho_1^*} D_1}; \quad \tilde{\delta}_1 = \frac{\delta_1}{1 + D_1}; \quad \tilde{\delta}_2 = \frac{\delta_2'}{1 + D_2'} \quad (14-16)$$

By using these effective rate constants the overall copolymerization rate equation for systems similar to St/DEM can be given as:

$$\frac{W_2}{\sqrt{W_1}} = \frac{\tilde{\rho}_1 m_1^2 + 2m_1 m_2}{\{\tilde{\delta}_1^2 \tilde{\rho}_1^2 m_1^2 + 2\phi \tilde{\delta}_1 \tilde{\delta}_2 \rho_1 m_1 m_2 + \tilde{\delta}_2^2 m_2^2\}^{1/2}} \quad (17)$$

The overall rate dependence on the initial monomer concentration is illustrated in Fig.2. The full curves in this Figure have been calculated on the basis of the hot radical theory by using the following parameter values of the polymerization of styrene in benzene:  $\delta_1 = 12.41$ ,  $\gamma_1 = 0.60$  and  $\gamma_{11} = 1.08$  [6]. Parameters not known from independent measurements were determined by a non-linear least squares treatment of all data. Experimental data allow the determination of only some combinations of the parameters of (17).

The best parameter values are:

$$\gamma_{12} = 2.0; \quad \phi \delta_2^1 \gamma_{22}^1 = 2.5; \quad \phi \delta_2^1 \gamma_{21}^1 = 0.75; \quad \phi \delta_2^1 \gamma_2^1 = 11$$

As it can be seen in Fig.2, the theoretical curves calculated with the aid of these parameter values give an excellent description of all experimental data.

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