Polymer Bulletin 28, 703–707 (1992)

Polymer Bulletin

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Easy use of Lewis and Mayo's rule to determine monomer conversion-rates in cotelomerization

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Summary : The Lewis and Mayo's rule, used so far for the determination of r_1 and r_2, is presently applied for the simultaneous determination of partial monomers conversions α_1 and α_2 ; whereas the integration of the Skeist's rule gave global conversion α only. An experimental verification is performed for the cotelomerization of MMA and maleic anhydride with dodecyl mercaptan as telogen, and it gives a very good correlation.

INTRODUCTION

For copolymerization it is well known, that the feed composition of the monomers directs the composition of the copolymer (O'BRIEN, 1955). However the $\overline{DP_n}$ of the copolymers cannot be predict as for homopolymerization because of the complexity of the general rule which links the $\overline{DP_n}$ to the concentration of reactants and rate constants (especially the unknow constant of cross termination). That produced a great limitation of the general copolymerization equation and usually empirical laws are used.

Our recent works in cotelomerization (BOUTEVIN, 1990) showed that it is interesting to use Tsuchida's law (TSUCHIDA, 1972), linking the instantaneous number-average degree of polymerization, $(\overline{DP_n})_i$, to the reactivity ratios r_1, r_2 and the transfer constants C_{T1}, C_{T2} of a telogen T with both monomers M_1 and M_2 :

$$(\overline{DP_n})_i = \frac{r_1 \; [M_1]^2 + r_2 \; [M_2]^2}{[T] \; (r_1.C_{T1}.\,[M_1] + r_2.C_{T2}.\,[M_2])} \qquad (1)$$

However the problem is more difficult for batch reactions. Actually the concentrations $[M_1]$, $[M_2]$ and $[T]$ vary all during the reaction and consequently $\overline{DP_n}$ decreases generally. So the real value of $\overline{DP_n}$, named $(DP_n)_{cum}$, is determined with difficulty. Actually, in cotelomerization as in copolymerization, no method is supplied to evaluate $[M_1]$ and $[M_2]$ values. In the present work we show a pratical application of Lewis and Mayo's rule (MAYO, 1944) to predict these variations and to compare them with the experimental results.

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RESULTS AND DISCUSSION

Skeist's rule permits to calculate the global monomer conversion, α, versus f_1 and F_1, the molar fraction of the M_i monomers in the mixture of monomers and in the copolymers, respectively (SKEIST, 1946):

$$\ln (1-\alpha) = \int_{f_1^o}^{f_1^t} \frac{1}{F_1-f_1} \, df_1 \qquad (2)$$

with $f_1 = [M_1] / ([M_1] + [M_2])$ and $F_1 = d [M_1] / (d [M_1] + d [M_2])$

f_1^o and f_1^t are the f_1 values at the beginning of reaction and at the considered time.

Before integration, several authors obtained the following formula (SPINNER, 1955) (MEYER, 1964) :

$$\ln(l-\alpha) = A \ln f_1^o/f_1^t + B \ln (f_1^o-1)/(f_1^t-1) + C \ln (f_1^o-a)/(f_1^t-a) \qquad (3)$$

with $A = r_1/(r_1-1)$; $B = r_2/(r_2-1)$; $C = (1-r_1.r_2)/(1-r_1)(1-r_2))$ and
$a = (r_2-1)/(r_1 + r_2-2)$.

It is very important to note that only global conversion can be obtained by this method but this is not the case for partial conversion α_1 and α_2. Moreover the only rule which links α which α_1 and α_2 is the following :

$$\alpha = f_1 . \alpha_1 + f_2 . \alpha_2 \qquad (4)$$

So the determination of α does not imply that α_1 and α_2 can be calculated. That is an other important limitation of copolymerization kinetics because only empirical (one more time) rules are used to perform half batch reactions, i.e. reactions which require an addition of both the monomers during the reaction.

The consequences of this two "mis understandings" are the derivative of copolymers composition and also of their $\overline{DP_n}$ values.

Our purpuse is to provide a rational method in order to avoid these problems.

In 1944, Lewis and Mayo (MAYO, 1944) integrated the general kinetic equation of copolymerization (Eq.5) and they obtained (Eq.6) :

$$d [M_1] / d [M_2] = ([M_1] / [M_2]). (r_1 . [M_1] + [M_2]) / (r_2 . [M_2] + [M_1]) \qquad (5)$$

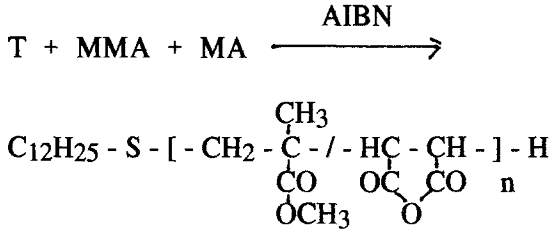
$$r_2 = \frac{\ln\frac{[M_2]_o}{[M_2]} + \frac{1}{p}\ln\left[\left(1-p\frac{[M_1]_o}{[M_2]_o}\right)/\left(1-p\frac{[M_1]}{[M_2]}\right)\right]}{\ln\frac{[M_1]_o}{[M_1]} - \ln\left[\left(1-p\frac{[M_1]_o}{[M_2]_o}\right)/\left(1-p\frac{[M_1]}{[M_2]}\right)\right]} \text{ with } p = \frac{1-r_1}{1-r_2} \qquad (6)$$

Here, $[M_1]_o$ and $[M_2]_o$ stand for the monomer-concentrations at the beginnng of the reaction.

Unfortunately the authors used eq.6 for the determination of the reactivities ratios r_1 and r_2 only.

On the contrary, when r_1 and r_2 values are known equation 6 enables us to correlate $[M_1]$ and $[M_2]$ values during the reaction. Thus we known the α_1 and α_2 values, without any aproximation.

In this paper, we propose to check this theory by using experimental data for the telomerization of maleic anhydride (MA) and methyl methacrylate (MMA) with dodecanethiol (T) as telogen.



$$T + MMA + MA \xrightarrow{AIBN} C_{12}H_{25}-S-[-CH_2-C(CH_3)(CO\,OCH_3)-/-HC-CH-]_n-H$$

The reaction, carried out at 75°C in THF, is followed by ^1H NMR measurements with an internal standard (ethyl formiate) which gives a singlet at 8.0 ppm. The comparisons between intensities of that peak and those of MA (singlet at 7.0 ppm) and of the double bond of MMA (two singlets at 5,6 and 6,1 ppm) allows the determination of $[M_1]$ and $[M_2]$, and thus of α_1 and α_2 (Tab.1).

Moreover, we have already calculated the values of r_1 and r_2 in a previous paper (BOUTEVIN, 1990) : r_1 = rMMA = O and r_2 = rMMA = 3,38.

For $[M_1]_o = [M_2]_o$ = 0,77 mol/L, Eq.6 :

$$3.38 = \frac{\ln(0.77/\ [M_2]\ ) - 2.38\ln\left[1.42/(1+0.42\ [M_1]\ /\ [M_2]\ )\right]}{\ln(0.77/\ [M_1]\ ) - \ln\left[1.42/(1+0.42\ [M_1]\ /\ [M_2]\ )\right]} \qquad (7)$$

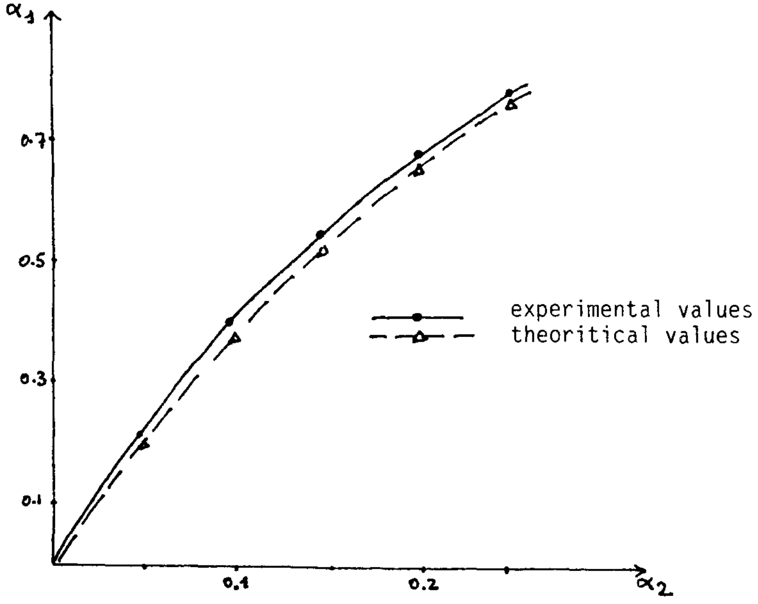
Table 1 : Experimental conversions of the cotelomerization of methyl methacrylate and maleic anhydride with dodecanethiol versus time.

time mn Monomer fractional conversion (α)	0	30	60	75	90	105
MMA	0	0.23	0.41	0.55	0.68	0.77
MA	0	0.05	0.10	0.15	0.20	0.25

Table 2 : Theoritical values of the fractional conversions α_1 versus α_2 according to the theoritical values of M_1 and M_2 calculated by the Eq. 7.

α_2	0	0.05	0.10	0.15	0.20	0.25
α_1	0	0.21	0.39	0.54	0.66	0.78

Figure 1 : Theorical (dotted line) and experimental (full line) values of α_1 and α_2.



For a given $[M_1]$ value, we compute $[M_2]$ by iteration. So choosen $[M_1]$ values give therotical conversion α_1 and calculated $[M_2]$ values give theoretical conversion α_2 (table 2).

The figure 1 represents the theoritical and experimental values of α_1 versus α_2. A very good correlation can be noted.

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Accepted April 25, 1992 C