Polymer Bulletin 2, 527–532 (1980)

Polymer Bulletin

Alternating Copolymerization of Phenylvinyl sec-Butyl Ether and Maleic Anhydride

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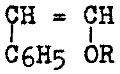
Dedicated to Prof. C.I. Simionescu in honor of this 60th birthday

SUMMARY

The reactivity ratios k_{1c}/k_{12} and k_{2c}/k_{21} in the copolymerization of phenylvinyl sec-butyl ether (M_2) and maleic anhydride (M_1) were calculated by applying the generalized model described by Shirota and coworkers. It was found that under the experimental conditions applied in our work, the copolymerization proceeds predominantly through the participation of charge-transfer complex monomers.

INTRODUCTION

A series of copolymers of phenylvinyl alkyl ethers (I) and maleic anhydride (MAn) was previously prepared in our laboratories, and it was proved that in all cases alternating copolymers were obtained (VUKOVIĆ et al. 1977,1979).



$$\underset{C_6H_5}{CH}=\underset{OR}{CH}$$

I

R = Me, Et, n-Pr, n-Bu, sec-Bu, CH(Me)Et, $CH_2CH(Me)Et$, $(CH_2)_2CH(Me)Et$.

It was further proved that the copolymerization reaction proceeds through the mechanism of charge-transfer complex monomers (CT-complex). Copolymerization was performed in benzene solution in the presence of AIBN as initiator. The equilibrium constants and activation energies in the free radical initiated copolymerization were proved to be independent on the steric factors, while the rate of reaction was largely influenced by the bulkiness of alkyl group (FLES et al. 1979).

In the present paper, we wish to report our recent results on the determination of relative reactivity of monomers and CT complex monomers respectively, with corresponding macroradicals in the copolymerization of I (R = sec-Bu) and MAn, and to compare these results with the data previously obtained in the copolymerization of I (R = Et) and MAn.

0170-0839/80/0002/0527/$01.20

EXPERIMENTAL

Phenylvinyl sec-butyl ether was prepared by condensation of phenylacetylene with sodium sec-butoxide as previously described (VUKOVIC and FLES, 1975). The copolymerization was performed in benzene with 0.4% AIBN at various electron donor-acceptor ratios, but at the same total monomer concentrations. The initial rate of copolymerization was determined gravimetrically.

RESULTS AND DISCUSSION

The mechanism of CT complex monomer copolymerization was studied by many workers, and several different models were proposed. It seems however that the mechanism which is based on the assumption that alternating copolymers are formed by simultaneous cross-propagation of free monomers and addition of CT complex monomers is prevailing. The determination of the relative participation of free monomers and CT complex monomers in the copolymerization reaction is based on the quantitative treatment of the initial rate of propagation described by SHIROTA et al. (1974), and applied in our previous work (FLES et al. 1979). Evaluation of the reactivity ratios is based on the change of copolymerization rate with monomer feed at constant total monomer concentration.

Figure 1 represents the plot of initial rate of copolymerization of I (R = sec-Bu) and MAn, against molar ratio of I (R = sec-Bu) in monomer feed at total monomer concentrations in feed 0.8, 2.0 and 4.0 mole/l respectively.

It is evident from Figure 1 that the maximum of the initial copolymerization rates are always located at higher concentrations of maleic anhydride in the feed, and are approaching the equimolar ratios of electron donor and acceptor with increasing the total monomer concentration in the feed.

By assuming that the overall initial rate of copolymerization is given by the sum of the rate of copolymerization of CT complex monomers $R_p(CT)$ and free monomers $R_p(f)$:

$$R_p = R_p(CT) + R_p(f) \qquad (1)$$

where

$$R_p(f) = k_{12}[m_1^{\bullet}][M_2] + k_{21}[m_2^{\bullet}][M_1] \qquad (2)$$

$$R_p(CT) = 2(k_{1c}[m_1^{\bullet}][CT] + k_{2c}[m_2^{\bullet}][CT]) \qquad (3)$$

$[M_1]$ and $[M_2]$ are molar concentrations of maleic anhydride and phenylvinyl sec-butyl ether respectively, $[CT]$ represents the molar concentration of charge-transfer complex monomers $[M_1M_2]$ and $[M_2M_1]$; $[m_1^{\bullet}]$ and $[m_2^{\bullet}]$ are molar concentrations of macroradicals having M_1 and M_2 ends, respectively.

By applying the steady state approximation to the copolymerization, it was shown that the ratio of $R_p/[M_1]$

is a first order function with respect to the concentration of $[M_1]$:

$$R_p/[M_1] = A(X)\cdot K\cdot(k_{1c}/k_{12} + k_{2c}/k_{21}\cdot X)[M_1] + A(X) \quad (4)$$

where K is the equilibrium constant of charge-transfer complex monomer = 0.3 l/mole; $X = [M_2]/[M_1]$; A(X) correlates the rate constants with X at steady state approximation.

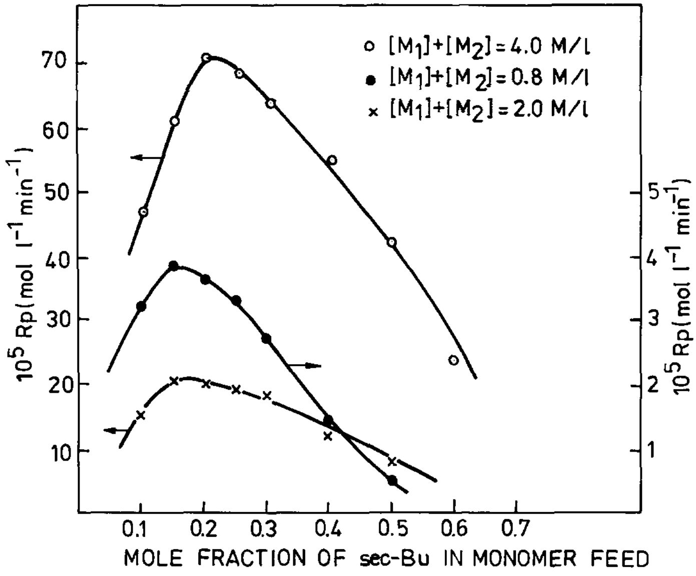


Figure 1. Initial copolymerization rate against monomer feed molar ratios in copolymerization of I (R = sec-Bu) and MAn; 0.4% AIBN at 70°C in benzene; a) I + MAn = 0.8 M; b) I + MAn = 2.0M; c) I + MAn = 4.0 M.

It is evident from equation (4) that $R_p/[M_1]$ against $[M_1]$ gives straight lines for each X. The slope of the straight lines is $A(X)\cdot K(k_{1c}/k_{12} + k_{2c}/k_{21}\cdot X)$ and the intercept represents A(X) (Figure 2).
If

$$K(k_{1c}/k_{12} + k_{2c}/k_{21}\cdot X) = F(X) \quad (5)$$

the plot of F(X) vs. X should give a straight line, the slope of which is $K\cdot k_{2c}/k_{21}$ and the intercept $K\cdot k_{1c}/k_{12}$ (Figure 3). The equilibrium constant was previously determined : K = 0.3 l/mole.
From Figure 3, reactivity ratios of the CT complex monomers to the free monomers are as follows :

$$k_{1c}/k_{12} = 0.55 \qquad k_{2c}/k_{21} = 33.33$$

$$k_{1c}k_{21}/k_{2c}k_{12} = 0.02$$

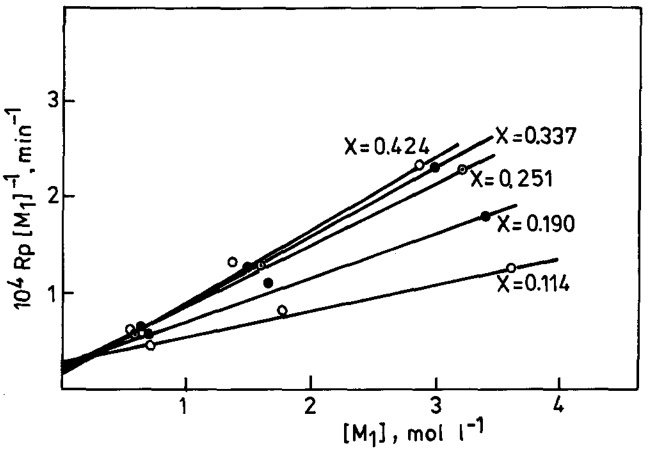


Figure 2. Plot of $R_p/[M_1]$ against $[M_1]$ at different $[M_2]/[M_1]$ ratios in the copolymerization of phenylvinyl sec-butyl ether $[M_2]$ and maleic anhydride $[M_1]$.

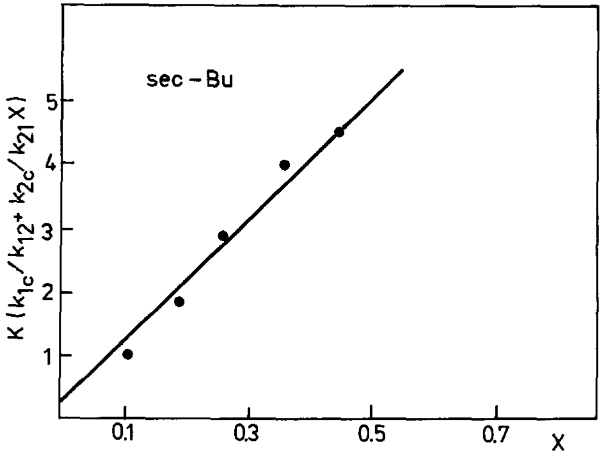


Figure 3. Plot of $K(k_{1c}/k_{12} + k_{2c}/k_{21}\cdot X) = F(X)$ against X in the copolymerization of phenylvinyl sec-butyl ether and maleic anhydride.

It is evident that in the copolymerization of I and MAn, the rate of formation of electron acceptor radicals ($k_{1c}k_{21}$) is slower than the rate of electron donor radicals ($k_{2c}k_{12}$), which is in agreement with the data previously described for the copolymerization of I (R = Et) and MAn.

From equation (1), the relative participation of $R_p(f)$ and $R_p(CT)$ was calculated and the results are shown in Figure 4.

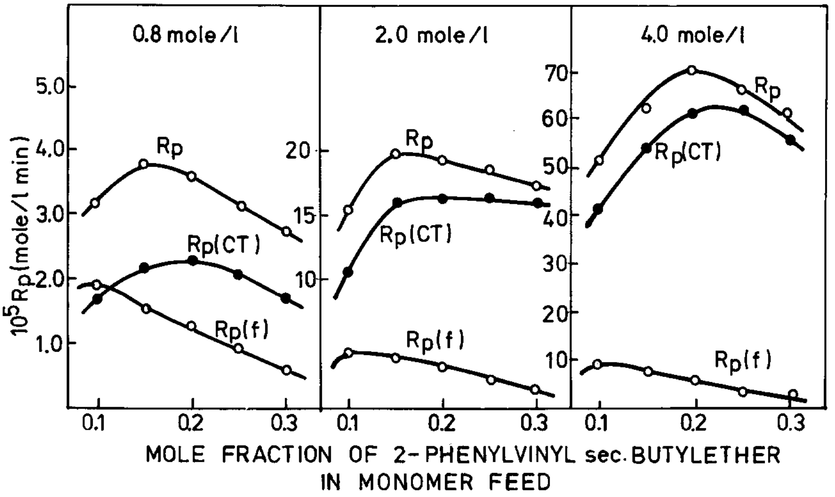


Figure 4. The relative participation of free monomers and CT complex monomers in the copolymerization of phenylvinyl sec-butyl ether and maleic anhydride at different monomer feed concentrations.

The data presented in Figure 4 indicate that in the range of total monomer concentration between 0.8 and 4.0 mole/l the copolymerization of I (R = sec-Bu) and MAn proceeds predominantly through the addition of charge transfer complex monomers. It is interesting to note that in the copolymerization of I (R = Et) and MAn at concentration of 0.8 mole/l the copolymerization proceeds predominantly via the cross propagation of free monomers, while at a concentration of 4.0 mole/l the reaction is almost entirely the homopolymerization of CT complex monomers (VUKOVIC et al. 1979). The difference in the relative participation of free monomers and CT complex monomers in the copolymerization of I (R = sec-Bu) and I (R = Et) with MAn could be due to the difference in the bulkiness of alkyl group in electron donor monomer.

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Received March 3, 198o