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Correlation Between Copolymerization Reactivity Ratios and Rates of Radical Additions to Alkenes

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SUMMARY

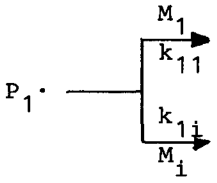
Rates of addition of cyclohexyl radicals to alkenes are measured using the "mercury method". These rates can be correlated with data of styrene copolymerization. Copolymerization reactivity ratios therefore describe relative reactivities of polymer radicals in addition reactions to alkenes. It turns out that the polymeric benzylic radicals are less selective than the cyclohexyl radicals.

INTRODUCTION

In radical copolymerizations of an alkene M_1 with different monomers M_i copolymerization parameters r_1 are the selectivities of polymeric radicals $P_1\cdot$ in competition reactions between M_1 and M_i

$$M_1 \longrightarrow P_1\cdot$$

$$M_i \longrightarrow P_i\cdot$$



$$r_1 = \frac{k_{11}}{k_{1i}}$$

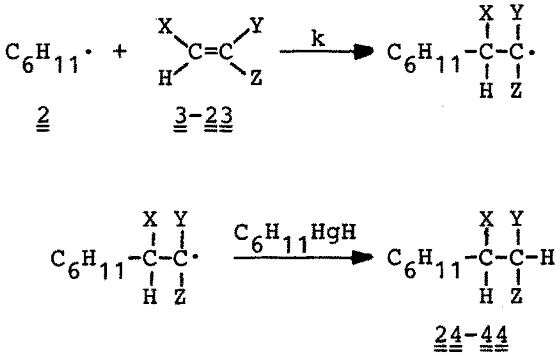
If penultimate unit effects of polymeric radicals $P_1\cdot$, 1:1 charge complexes of M_1 with monomers M_i and viscosity effects are of minor importance, the data $1/r_1$ should describe rel. rates of a radical $P_1\cdot$ in addition reactions to alkenes M_i.

To proof this we have measured rel. rates of the cyclohexyl radical $\underline{\underline{2}}$, using a recently developed "mercury method" (GIESE and MEISTER 1977a): Reduction of cyclohexyl mercuric chloride 1 with $NaBH_4$ generates alkyl radicals 2 (HILL and WHITESIDES 1974), that react with alkenes 3-23 via adduct radicals to yield products 24-44 (eq. a-e)

$$\underset{1}{C_6H_{11}HgCl} \xrightarrow{NaBH_4} C_6H_{11}HgH \qquad (a)$$

$$C_6H_{11}HgH \longrightarrow C_6H_{11}Hg\cdot + H\cdot \qquad (b)$$

$$C_6H_{11}Hg\cdot \longrightarrow \underset{2}{C_6H_{11}\cdot} + Hg \qquad (c)$$



$$\underset{2}{C_6H_{11}\cdot} + \underset{3-23}{XHC{=}CYZ} \xrightarrow{k} C_6H_{11}-\overset{X}{\underset{H}{C}}-\overset{Y}{\underset{Z}{C}}\cdot \qquad (d)$$

$$C_6H_{11}-\overset{X}{\underset{H}{C}}-\overset{Y}{\underset{Z}{C}}\cdot \xrightarrow{C_6H_{11}HgH} \underset{24-44}{C_6H_{11}-\overset{X}{\underset{H}{C}}-\overset{Y}{\underset{Z}{C}}-H} \qquad (e)$$

In competition reactions with couples of alkenes rel. rates of cyclohexyl radicals 2 can be determined from analysis of the products (GIESE and MEISTER 1977b).

EXPERIMENTAL

About 0.3 mmol of cyclohexyl mercuric chloride 1 and couples of 3-300 mmol of alkenes 3-23 were dissolved in 10-30 ml CH_2Cl_2. At 20°C 0.5 - 1.5 mmol $NaBH_4$ in 0.5 - 2.0 ml H_2O was added. After 5-30 min the mixture was filtered and analysed by gas chromatography. From the ratio of alkenes 3-23 and products 24-44 rel. rates of additions are calculated (TABLE 1).

RESULTS and DISCUSSION

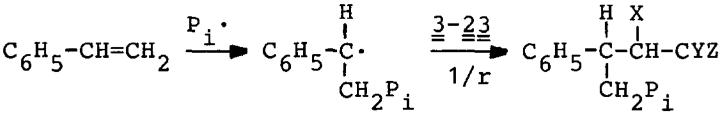
The rel. rates of additions of cyclohexyl radicals 2 to alkenes 3-23 and the copolymerization ratios 1/r of styrene copolymerizations (YOUNG 1975) are compiled in TABLE 1.

TABLE 1

Rel. rates of cyclohexyl radicals 2 (k, 20°C) and copolymerization ratios (1/r, 60°C) of styrene copolymerizations with alkenes 3-23.

	X	Y	Z	k	1/r	log k	- log r
3	CO_2CH_3	H	C_6H_5	0.4	0.5	- 0.40	- 0.30
4	H	H	C_6H_5	= 1.0	= 1.0	= 0.00	= 0.00
5	H	OCH_3	CO_2CH_3	1.1	0.9	0.03	- 0.04
6	H	Cl	Cl	1.2	0.5	0.08	- 0.30
7	H	H	p-ClC_6H_4	1.4	0.6	0.15	- 0.23
8	H	OC_2H_5	CN	3.3	2.5	0.52	0.40
9	H	C_6H_5	C_6H_5	3.4	2.5	0.53	0.40
10	H	CH_3	CO_2CH_3	5.0	2.0	0.70	0.30
11	H	H	CO_2CH_3	6.7	1.4	0.82	0.15
12	H	$CH_2CO_2CH_3$	CO_2CH_3	9.3	1.3	0.97	0.09
13	H	CH_3	CN	13	2.9	1.1	0.45
14	H	H	CN	24	2.5	1.4	0.40
15	CO_2CH_3	H	CO_2CH_3	30	3.3	1.5	0.52
16	H	C_6H_5	$CO_2C_2H_5$	43	15	1.6	1.2
17	H	Cl	CO_2CH_3	80	13	1.9	1.1
18	Methylmaleic anhydride			147	6.7	2.17	0.84
19	H	Cl	CN	207	14	2.31	1.15
20	H	$CO_2C_2H_5$	$CO_2C_2H_5$	273	33	2.44	1.52
21	H	C_6H_5	CN	440	50	2.64	1.70
22	Maleic anhydride			733	35	2.86	1.52
23	H	CN	CO_2CH_3	2067	100	3.31	2.00

The data in TABLE 1 demonstrate that substituents of alkenes 3-23 have more or less proportional effects on the reactivity log k of cyclohexyl radicals 2 (eq. d) and on the copolymerization data -log r of styrene copolymerizations (eq. f). Therefore radical copolymerizations are controlled by the same effects as additions of small alkyl radicals to alkenes. This leads to a linear free energy relationship (eq. g)



$$C_6H_5\text{-}CH{=}CH_2 \xrightarrow{P_i\cdot} C_6H_5\text{-}\overset{H}{\underset{CH_2P_i}{C}}\cdot \xrightarrow[1/r]{3\text{-}23} C_6H_5\text{-}\overset{H}{\underset{CH_2P_i}{C}}\text{-}\overset{X}{C}H\text{-}CYZ \qquad (f)$$

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$$-\log r = 0.58 \log k - 0.16 \qquad (g)$$

The proportionality factor of 0.58 (correlation coefficient = 0.92) of eq. (g) shows that cyclohexyl radicals 2 are more selective than benzylic radicals 45. This can be explained by a higher nucleophilicity of cyclohexyl radicals (GIESE and MEISTER 1977a, GIESE and MEIXNER 1980, CARONNA et.al. 1977) compared to a benzylic radical, which is substituted by an electron withdrawing phenyl group.

From eq. (g) copolymerization reactivity ratios r of styrene copolymerizations with alkenes M_i can be determined from measurements of rates k of cyclohexyl radicals. If steric effects become important the 1/r data might be smaller than predicted by the k values, because the rate of the more bulky polymer radical 45 should be retarded by steric effects to larger extend than the rate of the small cyclohexyl radical 2.

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