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The Reactivity of Polystyryl Radicals Towards Various Alkyl Substituted Styrenes

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Introduction

The effect of alkyl substitution on the reactivity of styrene in radical copolymerisations with several monomers has been reviewed by YOUNG (1964). However, the amount of quantitative data on the relative reactivity of styrene and substituted styrenes towards polystyryl radicals in this review, and in more recent literature, is very limited. Moreover, in many cases different conditions are applied so that direct comparison of the data available is impossible.

We report here on the reactivities of 15 different alkyl-substituted styrenes toward polystyryl radicals. These reactivities have been measured in copolymerisations of styrene with small amounts of the alkyl substituted comonomers under standard conditions.

Experimental

Styrene suspension polymerisations (i.e. droplet bulk polymerisations) were carried out at 90 °C employing 0.375 %w of benzoyl peroxide initiator and 0.3-0.5 %w (on total styrenes) of the comonomer to be studied.

Total conversion was determined by precipitation and the concentration of comonomer was determined by GLC relative to an internal standard included in the polymerisation recipe. Intrinsic viscosities of the polymers obtained at the end of the kinetic runs were determined, but no differences were observed that could suggest consumption of any of the comonomers in chain transfer reactions to such an extent as to influence the value of the reactivity ratio.

Experimental details of the polymerisation procedure and of the analyses are reported in our study of the copolymerisation of styrene and divinylbenzenes (KWANT, 1978).

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Results and discussion

If the concentrations of an alkyl substituted styrene (M_1) and styrene (M_2) are chosen such that the concentration of comonomer-tipped propagating radicals can be neglected compared to that of styrene-tipped radicals, the copolymerisation equation simplifies to:

$$d[M_1]/d[M_2] = 1/r_2 \times [M_1]/[M_2] \qquad (1)$$

r_2 being the appropriate reactivity ratio.

This equation can be integrated to give:

$$\log [M_1]/[M_1]_o = 1/r_2 \log [M_2]/[M_2]_o \qquad (2)$$

in which the subscript o indicates a starting concentration.

Analysis of samples of the polymerising mixture taken at regular intervals during a kinetic run provided $[M_1]$ and $[M_2]$, which, together with the starting concentrations, gave the data pair, $\log [M_1]/[M_1]_o$ and $\log [M_2]/[M_2]_o$. Linear regression analysis was applied to find the reactivity ratio r_2 from all the data pairs for a particular comonomer M_1. The standard error for each r_2 value was calculated from the regression equation and the data pairs. The results are presented in the Table.

TABLE

Radical copolymerisation of alkyl substituted styrenes (M_1) with styrene (M_2) at 90 °C

Comonomer (M_1)	No. of kinetic runs	No. of data pairs	r_2
Styrene			1
2-methylstyrene	3	44	0.90 ± 0.09
3-methylstyrene	2	48	0.82 ± 0.04
4-methylstyrene	2	31	0.82 ± 0.04
4-ethylstyrene	2	30	0.90 ± 0.04
4-isopropylstyrene	1	16	1.06 ± 0.07
4-t-butylstyrene	3	53	0.89 ± 0.03
2,4-dimethylstyrene	2	31	1.02 ± 0.03
2,5-dimethylstyrene	3	47	1.00 ± 0.04
2,6-dimethylstyrene	2	34	>5
2,4,6-trimethylstyrene	2	31	3.6 ± 0.6
α-methylstyrene	2	27	0.98 ± 0.07
α-methyl-4-isopropylstyrene	2	33	1.12 ± 0.07
α,β-dimethylstyrene	1	14	>3
β,β-dimethylstyrene	1	13	>5
Indene	1	8	5.1 ± 1.3

Direct comparison with reactivity ratios from literature sources is possible only in a limited number of cases. The experimental value for r_2 in the case of 4-methylstyrene (M_1), 0.82 ± 0.04 at 90 °C, can be compared with a literature value of 0.83 at 63 °C, obtained in a bulk copolymerisation (WILEY, DAVIS, 1960). The r_2 for the 4-isopropylstyrene case, 1.06 ± 0.07, is in the same range as 1.11 ± 0.01, measured earlier in bulk at 50 °C by BRAUN and KEPPLER (1964). At 70 °C, also in a bulk polymerisation, WILEY and JIN (1969) found r_2 values of 1.22 or 1.37 depending on the way the value is calculated. The data on 4-isopropylstyrene agree in that the r_2 values indicate a lower reactivity towards polystyryl radicals than for styrene itself.

The r_2 value for α-methyl styrene, 0.98 ± 0.07, is essentially the same as that for styrene which is in line with the reported indication that addition of free radicals, per se, is not hindered by the α-methyl group. However, the experimental results obtained in the past are difficult to interpret because of depolymerisation reactions of α-methylstyryl radicals (YOUNG, 1964). FISCHER (1972) reports r_2 values over a range of temperatures and his calculations account for the reversible addition of α-methylstyrene to α-methylstyryl tipped radicals. At 90 °C he reports r_2 to be 1.09.

Conclusions

Apart from the comparisons with literature data, the Table allows the following conclusions to be drawn concerning the effect of alkyl substitution on the reactivity of styrenes towards polystyryl radicals.

The presence of an alkyl group in the 4-position generally causes an increase in reactivity. The size of this alkyl group has no significant influence on reactivity. The fact that 4-isopropylstyrene is slightly less reactive than the other 4-substituted styrenes cannot yet be explained satisfactorily.

Methyl substitution at the 2-position alone does not result in a major reduction of reactivity. Methyl substitution at both the 2 and 6 positions, however, drastically reduces reactivity suggesting a strong steric effect. The latter conclusion is in line with that made earlier from results of a methyl affinity study by CARROCK and SZWARC (1959).

Substitution of styrene at the β position results in a considerable reduction of reactivity as illustrated by the last three r_2 values in the Table. Here, too, the reactivity towards polystyryl radicals is in line with the results of the above mentioned methyl affinity study.

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