THE EFFECT OF SUBSTITUTION ON THE REACTIVITY OF THE MONOMER IN THE COPOLYMERIZATION OF STYRENE WITH 2,3-UNSATURATED ALDEHYDES AND KETONES

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The monomer reactivity ratios of the copolymerization of styrene with propenal, 2-methylpropenal, 2-ethylpropenal, methylvinyl ketone and methylisopropenyl ketone were determined and their reliability was checked. For copolymerizations conducted to low conversions, a simple procedure was proposed in order to rule out the effect of the conversion heterogeneity of copolymers on the determination of r_1, r_2 by calculation using a differential copolymerization equation. When comparing aldehydes and ketones with reference monomers having a similar skeleton of the molecule, the effect of substitution on the monomer reactivity in the copolymerization was examined, and a new correlation, $e \sim \sigma^n$, was suggested, interpreting the influence of polar effects of substituents on the monomer reactivity. It was proved that the copolymerization kinetics of 2-ethylpropenal is affected by the steric hindrance from the part of the too bulky substituent.

The high reactivity of the carbonyl group makes copolymers of unsaturated aldehydes suitable for a wide range of applications[1-3]. The synthesis of copolymers of a desired composition requires knowledge of the general characteristics of behaviour of the monomers used. This is why this study is concerned with a detailed investigation of the copolymerization of propenal, 2-methylpropenal and 2-ethylpropenal with styrene, which because of the electronegativity of their carbonyl group is a suitable reference monomer for 2,3-unsaturated aldehydes. Earlier studies of polymers of propenal and its homologs[4,5] have revealed that the structure of these polymers is complicated by the formation of secondary hydrated structures with predominating cyclic hemiacetals

$$R = H, CH_3, C_2H_5$$
$$n = 1-4\,(5)$$
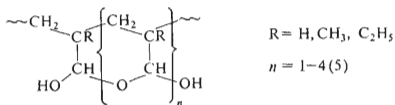
In view of this complication, the study also included two analogous ketones, the copolymers of which do not undergo such changes, *viz.*, methylvinyl ketone and methylisopropenyl ketone. No analogous ketone was available for 2-ethylpropenal. Using a comparative approach, we tried to find out if the complicated structure of copolymers of aldehydes partly formed already during the polymerization, even in an anhydrous medium[6], affected the copolymerization kinetics.

EXPERIMENTAL

Chemicals

Styrene (Kaučuk, Kralupy nad Vltavou) was repeatedly extracted with water, dried with an-hydrous calcium chloride and rectified *in vacuo* on a packed column, ⌀ 25 mm and 8 theoretical plates at the reflux ratio >50 : 1, which provided purity (GC) higher than 99·7%, b.p. 45·7°C/2·67 kPa, $n_D^{25} = 1·5440$. The water content determined by the K. Fischer was max. 0·01 wt.%.

Propenal (Dr Th. Schuchardt, FRG), 2-methylpropenal (Spolana Neratovice) and 2-ethyl-propenal (prepared from butanal by the Mannich reaction[7]) were dried on a molecular sieve 5A and rectified on a packed column ⌀ 25 mm and 17 theoretical plates at the reflux ratio >20 : 1, which removed the main part of impurities. The fractions used had the following b.p.'s and purity (GC): propenal: 33·4°C/50 kPa, >99·6%; 2-methylpropenal: 40·8°C/40 kPa, >99·9% and 2-ethylpropenal: 93°C/100 kPa, >99·5%. The water content determined by the cyanide method according to K. Fischer was max. 0·02 wt.% in all cases.

Methylvinyl ketone was obtained by the aldol condensation of acetone with formaldehyde, followed by the dehydration of 4-hydroxy-2-butanone thus formed according to ref.[8]. Methyl-isopropenyl ketone was prepared by the thermal decomposition of the product of the Mannich reaction of butanone with formaldehyde according to ref.[9]. Both ketones were dried with an-hydrous calcium chloride and rectified on the same column as aldehydes at the reflux ratio >30 : : 1. The fractions used were: methylvinyl ketone, b.p. 54·5°C/40 kPa, $n_D^{25} = 1·4100$, according to GC >99·9%, methylisopropenyl ketone, b.p. 95°C/100 kPa, $n_D^{25} = 1·4230$ and purity (GC) <99·4%.

2,2′-Azobis(isobutyronitrile) ("Porofor" — Lachema Brno) was recrystallized four times in advance and crystallized each time again prior to use, always from diethyl ether; m.p. 103°C (with decomposition).

Polymerization

The bulk polymerization was carried out in sealed tubes, approx. 13 ml in volume, at 55 ± 0·1°C, with 2,2′-azobis(isobutyronitrile) (0·3 mol.%) as initiator. Before sealing, oxygen was removed from the mixture in the tube by repeated freezing in a liquid nitrogen bath, followed by evacua-tion to 0·01 kPa, and the tubes were sealed under nitrogen. On reaching an approx. 5% conver-sion, the polymers were isolated from the reaction mixture by precipitating the ampoule contents into heptane or light petroleum (b.p. 40—70°C) and dried to constant mass at room temperature and 0·1 kPa.

RESULTS AND DISCUSSION

The composition of copolymers of styrene (M_1) with 2,3-unsaturated aldehydes and ketones (M_2) was calculated from the carbon content determined by elemental

analysis. The monomer reactivity ratios (r) were calculated using a differential copolymerization equation by the method of nonlinear regression[10], after the first estimates of r_1 and r_2 were obtained by a method suggested by Joshi and Joshi[11]. The effect of conversion heterogeneity of the copolymer composition on the calculation of r_1 and r_2 was compensated using a procedure where the calculation did not start from the initial composition of the mixture of monomers, but from average concentrations determined from the composition of copolymers and from the degree of conversion. The results are summarized in Table I. The reliability of the monomer reactivity ratios determination is best expressed by joint confidence limits[10] for the probability $\alpha = 0.05$ (95% joint confidence limits) plotted in Fig. 1.

The effect of this compensation procedure was corroborated by the calculation of r_1, r_2 using the integrated form of the copolymerization equation[12], modified by the Joshi and Joshi procedure[11] for the search of a solution by the least squares method. The calculated results were identical to those calculated by the linearization method[11] using the differential copolymerization equation and compensation of the conversion heterogeneity of composition. The fit of the results was perfect also for the values of estimated standard errors $(s_r^2)^{0.5}$. Without compensation of the heterogeneity of composition described above the use of the differential copolymerization equation gives distorted results, as evidenced by Fig. 1.

The monomer reactivity ratios published earlier for the monomeric pairs investigated in this study[13-19] are out of the determined joint confidence limits (Fig. 1). These differences can only in part be assigned to the expense of random experimental errors; the experimental conditions are of essential importance in this case. For

TABLE I

Determination of the monomer reactivity ratios and $Q-e$ values for the copolymerization of styrene with carbonyl monomers (M_2) of the type $CH_2=C(R')-CO.R$. Calculation with the compensation of conversion heterogeneity: A the linearization method[11], B nonlinear regression[10], i number of experimental points

M_2		i	A		B		Q_2	e_2
R	R'		r_1	r_2	r_1	r_2		
H	H	14	0.10 ± 0.04	0.30 ± 0.05	0.11	0.28	2.06	1.07
H	CH_3	35	0.17 ± 0.04	0.62 ± 0.12	0.14	0.53	1.92	0.80
H	C_2H_5	17	0.19 ± 0.03	0.46 ± 0.05	0.20	0.46	1.44	0.74
CH_3	H	14	0.23 ± 0.04	0.24 ± 0.03	0.22	0.23	1.13	0.92
CH_3	CH_3	13	0.35 ± 0.07	0.31 ± 0.03	0.36	0.31	0.85	0.68

instance, in ref.[16] the procedure used in the isolation of copolymers of styrene with 2-methylpropenal, *i.e.* extraction with boiling methanol for several hours, leads to a systematical error. We reproduced the reported isolation procedure and noticed a subsequent relative decrease in the carbon content in the copolymers due to acetalization proved by IR spectroscopy. This apparent rise in the content of 2-methylpropenal in the copolymers explains the results of determination of r_1 and r_2 in ref.[16]. Some differences may be due to variation in the polymerization conditions, such as temperature and solvent[20]; not all of the results are corroborated by reliable experimental data. *E.g.*, in ref.[13] the scatter of the composition of copolymers of styrene with propenal seems to be too small in view of the usual experimental error of the analytical method employed.

In our study we used the relatively high number of experimental points and the calculation procedure exceeding[10,21] methods used in the papers reported above. It justifies us to believe that the results summarized in Table I are indeed very close to correct values. This is also confirmed by the small areas corresponding to 95% joint confidence limits.
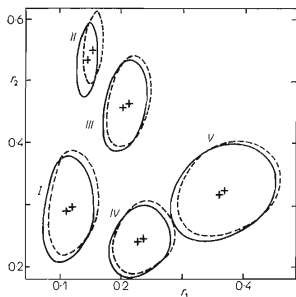

Fig. 1

The monomer reactivity ratios and 95% joint confidence limits: M_1 styrene, M_2: propenal (*I*), 2-methylpropenal (*II*), 2-ethylpropenal (*III*), methylvinyl ketone (*IV*), methylisopropenyl ketone (*V*). Calculation with the compensation of conversion heterogeneity — solid curve, calculation using the initial concentrations of monomers — dashed line
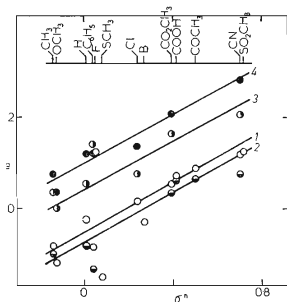

Fig. 2

Correlation of the *e*-values of monomers with the σ^n constants of substituents: ○ monosubstituted ethylenes (*I*), ◒ 2-substituted propylenes (*2*), ◑ 2-substituted acrylates (*3*), ● 2-substituted acrylonitriles (*4*)

In the series of monomers investigated, the pronounced $-M$ effect of the $C=O$ group reduces the electron density on the $C=C$ bond, thus raising its reactivity towards the polystyrene radical. This effect is to some extent compensated by the $+I$ effect of the alkyl substituent. This is why the relative reactivity $(1/r_1)$ of aldehydes towards the polystyrene radical is higher than that of ketones, and that of monomers less substituted with alkyls is higher than the one of those more substituted (Table II). Among the monomers compared the aldehydes are most reactive and also show the most pronounced trend towards alternation in the copolymerization with styrene (the lowest values of $r_1 \cdot r_2$ with the exception of the pair stryene/acrylonitrile).

The effect of substitution on the monomer reactivity can be quantitatively described by linear correlation of free energies, as did, e.g., Yamada and Otsu[22]. They correlated the e-values from the $Q-e$ scheme with the σ_p constants of the Hammett equation while separating from each other the influences of the polar and resonance effects of substitution on the reactivity of 2-substituted acrylates and acrylonitriles. On the other hand, Kieboom[23] criticized the use of σ_p constants for these purposes and the extension of the Hammett equation to include further socalled "resonance" terms connected with it. He showed that all such modifications of the Hammett equation[22,24-26] can be replaced by rewriting the original equation to

$$\log\left(k_{(X)}/k_{(O)}\right) = \varrho(\sigma^n + r^+ \, \Delta\overline{\sigma_R^+} + r^- \, \Delta\overline{\sigma_R^-}), \qquad (1)$$

TABLE II

Relative reactivities $(1/r)$ and tendency towards alternation $(r_1 \cdot r_2)$ in the copolymerization of styrene with monomers of type $CH_2=C(R')-X$ in the bulk or in solution at $50-90°C$

$f(r)$	R'	X				
		CO.H	CO.CH$_3$	CO.OCH$_3$	CO.OH	CN
	H[a]	9·17	4·44	1·21—1·33	4·0 —6·67	3·12--3·0
$1/r_1$	CH$_3$[a]	6·90	2·79	1·85—2·27	6·67	2·33—4·0
	C$_2$H$_5$	4·95	—	1·22[b]	—	—
	H[a]	3·57	4·27	5·0 —6·67	2·22—4·0	14·3
$1/r_2$	CH$_3$[a]	1·88	3·21	2·0 —2·38	1·43	3·57—6·25
	C$_2$H$_5$	2·19	--	4·76[b]	—	—
	H[a]	0·0305	0·0527	0·140	0·070	0·0105
$r_1 \cdot r_2$	CH$_3$[a]	0·0772	0·1120	0·250	0·105	0·690
	C$_2$H$_5$	0·0924	—	0·172[b]	—	---

[a] Data from ref.[30] for X: CO.OCH$_3$, CO.OH, CN. [b] Data from ref.[29]

which has been derived earlier by Yukawa and coworkers[27] (cf. ref.[23]). Here, the subscript in brackets denotes the substituent. The use of σ^n constants instead of the usual σ_p eliminates the effect of the heterolytic resonance interaction[28], and the quantities r^+ and r^-, or of $\Delta\overline{\sigma_R^+}$ and $\Delta\overline{\sigma_R^-}$ are the resonance parameters of the reaction or of the substituents, respectively. At the same time, the values $\Delta\overline{\sigma_R^+}$ and $\Delta\overline{\sigma_R^-}$ are obtained as the difference $\sigma_p^+ - \sigma^n$, or $\sigma_p^- - \sigma^n$, respectively.

This paper reports an attempt to carry out a new correlation of the e-values with the σ^n-constants. It was found that the correlation can be described by

$$e_{2(X)} = 2\cdot4\sigma^n_{(X)} + e_{2(O)}, \tag{2}$$

similarly to the expression derived by Yamada and Otsu for the correlation $e \sim \sigma_p$ for a narrower series of mononers. The ketones under study are very close to the correlation straight lines, as can be seen in Fig. 2. Aldehydes could not be included, however, because the σ^n constant of the —CHO group has not been published yet. According to Fig. 2, the e values determined in this study for propenal and 2-methylpropenal would have their corresponding value in $\sigma^n_{(CHO)} = 0\cdot6$. However, the aldehydes investigated in this study do not satisfy a similar correlation $e \sim \sigma_p$, and the group —CHO does not satisfy the otherwise very adequate correlation $\sigma^- = 1\cdot582\sigma_p - 0\cdot013$, determined for this type of substituents with the —M effect[23]. Hence, we can expect an anomalous behaviour of aldehydes during copolymerization, not necessarily connected with the above mentioned complicated structure of the copolymers.

Using Eq. (2), Yamada and Otsu[22] derived for $\sigma_{p(X)}$ the equation

$$\log(k_{12(X)}/k_{12(O)}) = 0\cdot83\sigma_{p(X)} + \log(Q_{2(X)}/Q_{2(O)}), \tag{3}$$

where $k_{12(X)}/k_{12(O)}$ is the ratio of relative reactivities $1/r_1$ of the X-substituted mononer and unsubstituted monomer (M_2) with respect to the polystyrene radical, and $\log(Q_{2(X)}/Q_{2(O)})$ is a change in $\log Q_2$ related to the introduction of the substituent X into the monomer $M_{2(O)}$. Since Eq. (2) holds also for σ^n, it can be written that

$$\log(Q_{2(X)}/Q_{2(O)}) = 0\cdot83(r^+\,\Delta\overline{\sigma_R^+} + r^-\,\Delta\overline{\sigma_R^-}). \tag{4}$$

Substitution of known values into the left-hand and right-hand sides of Eq. (4) should then make possible calculation of the resonance parameters of reaction, r^+ and r^-. In fact, however, such a procedure leads to different r^+ and r^- in each particular case, so that this approach does not solve the problem completely.

If the size of the alkyl group in position 1- of 1,1-disubstituted ethylene increases, the increasing $+I$ effect along with the steric effect should lead first to a decrease

in reactivity with respect to the reference radical, second, to a decrease in the trend towards alternation in the copolymerization with styrene and third, to a decrease in the e-value of this monomer. The validity of this reasoning has been corroborated by the results measured both for aldehydes and for ketones. In ref.[29], changes in the relative reactivity of methyl-2-alkyl acrylates connected with a change in the size of the alkyl substituent were investigated, and a departure was observed from what has been said above after the methyl group was introduced into position 2- in methyl acrylate. Nitriles and acids listed in Table II behave in a similar way. The finding that no such departure could be seen in aldehydes is obviously in no connection with the specific structure of copolymers of aldehydes, because substitution in a series of ketones has the same effect.

Steric hindrance becomes operative in 1,1-disubstituted ethylenes if the substituents are bulkier than the methyl group. In these cases the monomer homopolymerizes reluctantly, and in the copolymerization with styrene (M_1) unexpectedly low r_2 values appear[29]. This indicates unwillingness to form long homosequences of the monomer M_2. Such a behaviour was observed in this study with 2-ethylpropenal: the homopolymer could not be prepared at all, and r_2 was lower than r_2 of 2-methylpropenal. This demonstrates that in addition to polar and resonance effects, the behaviour of 2-ethylpropenal is also affected by the steric hindrance of the too bulky substituent in position 2-.

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