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Reexamination of the Stereospecific Copolymerization of Butadiene with Isoprene

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SUMMARY

14 systems of the stereospecific anionic butadiene/isoprene copolymerization were reinvestigated using the Kelen-Tüdős (KT) treatment of data. It was found that the classical binary copolymerization model holds for these systems, too; the level of error is relatively moderate and the reproducibility is better than in case of cationic copolymerizations.

INTRODUCTION

In earlier publications (KENNEDY et al. 1975), we reported the results of the reexamination of cationic copolymerization systems. This work was done by the Kelen-Tüdős (KT) method. It was demonstrated that the KT equation (KELEN and TÜDŐS 1974, 1975), derived originally for free-radical binary copolymerization systems (ALFREY and GOLDFINGER 1944, MAYO and LEWIS 1944), can be applied equally well to cationic systems. By the use of the KT equation we determined, for systems with reliable data base, accurate $\underline{r}$ values and, using the KT plots, checked the validity of assumptions implicit in the classical formulation of binary copolymerization. The visual evaluation of the plots made it possible to arrange the reexamined systems into three classes (I and I(!) = linear systems, II = systematic deviation from linearity, III = unreliable systems or erroneous data).

The KT equation is based on the differential form of the classical copolymerization equation, thus, originally, its applicability was restricted to experimental data obtained at low conversions. In its extended form (TÜDŐS et al. 1975, 1976), however it can be used with high conversion data as well. This modification has substantially extended the data base for the comprehensive reevaluation of copolymerization experiments, preserving at the same time the advantages of the linearization technique. The calculation method of the reactivity ratio confidence intervals was published separately (KELEN et al. 1980)

In our laboratories a comprehensive and critical reexamination of anionic stereospecific copolymerization experiments is in progress. The results obtained by the evaluation of butadiene/isoprene copolymerizations, presented in this paper, may illustrate the general features of this type of copolymerization.

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Table I

Data for butadiene(1)/isoprene(2) copolymerizations

No.	Catalyst system	Mole ratio	Solvent	Temp. °C	Original		Ref.	Recalculated		r_1r_2	$\delta^{\square}$	Class	Remark
					r_1	r_2		r_1	r_2				
1.	$TiCl_4/AlEt_3$	1/1.25	hexane	1-3	1	1	1	0.674±0.205	0.873±0.336	0.588±0.405	0.117	I(!)	
2.	$TiCl_4/AlEt_3$	1/1.5	benzene	21	1.6	1.1	2	1.304±0.529	0.565±0.314	0.737±0.708	0.225	I(!)	a,b
3.	$TiCl_4/AlEt_3$	1/1.5	benzene	15	1.49	1.3	2	1.216±0.316	0.936±0.387	1.138±0.766	0.107	I	c
4.	$TiCl_4$/Al iBu_3	1/1.1	benzene	30	1.0±0.05	1.0±0.05	3	1.042±1.888	1.060±1.895	1.105±3.976	3.230	I(!)	c
5.	$TiCl_4$/Li nBu	1/5	benzene	40	1.6±0.3	0.8±0.2	4	1.227±0.852	0.568±0.954	0.697±1.654	1.166	I(!)	
6.	$TiJ_4/AlEt_3$	1/5	benzene		1.88	0.55	2	1.828±0.162	0.560±0.174	1.024±0.409	0.027	I	d
7.	$Co(acac)_2/AlClEt_2$	1/1133	toluene	-15 +48	1	1	5	0.998±0.033	0.986±0.060	0.984±0.092	0.002	I	e
8.	$CoCl_2\cdot EtOH$/AlCi iBu_2		benzene	30	2.3±0.1	1.15±0.05	3	2.382±0.588	1.200±0.344	2.858±1.525	0.071	I	
9.	$CoCl_2\cdot EtOH/AlClEt_2$	1/200	benzene		0.92±0.05	1.25±0.18	6	0.776±0.252	1.150±0.289	0.892±0.514	0.082	I	
10.	$CoCl_2\cdot Py/AlClEt_2$	1/140	benzene	17	0.99±0.03	1.37±0.03	6	0.868±0.312	1.201±0.268	1.042±0.607	0.080	I	
11.	$NiCl_2\cdot Py/AlClEt_2$		benzene	30/15	1.15±0.02	0.59±0.02	6	1.128±0.179	0.606±0.173	0.684±0.304	0.045	I	
12.	$Cr(allyl)_3$/Al silicate		toluene	70	1.06±0.05	0.8±0.05	7	1.234±0.169	0.812±0.078	1.002±0.233	0.013	I	
13.	Cr_2O_3/Al silicate		toluene	70	1.04±0.05	0.76±0.05	7	1.029±0.258	0.717±0.172	0.738±0.362	0.060	I	
14.	Nd stearate/ /$AlClEt_2$/Al iBu_3	Nd/Cl/Al = = 1/2/30	toluene	25	1.94	0.62	8	2.047±0.521	0.611±0.272	1.251±0.875	0.113	I(!)	a

Remarks: a: the possibility of systematic deviation (Class II) cannot be excluded; b: catalyst untreated; c: catalyst washed; d: two data points omitted; e: various experimental temperatures

RESULTS AND DISCUSSION

In the literature we have found 14 systems of stereospecific anionic butadiene/isoprene copolymerization, giving reliable results on recalculation. The characterization of the reaction systems, the reactivity ratios given in the original publications and the results of our calculations are summarized in Table I.

A typical KT plot is given in Fig.1, illustrating one of the systems studied (N° 11 of Table I).

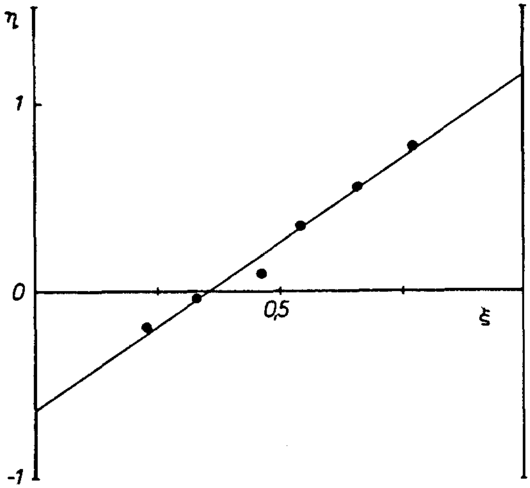

Figure 1. KT plot of System 11 of Table I.

In Fig.2 the reactivity ratios, their 95% confidence intervals and the joint r_1,r_2 95% confidence areas are given for the same system, obtained by the KT and the nonlinear least squares method, respectively. (In case of the latter, the sum of the squared deviations of the molar copolymer composition from the calculated values was minimized). The results obtained by the different methods are practically identical, showing the near equivalence of these estimations. Comparing the reactivity ratios given in the original publications with the ones determined by us (Table I), we can state that the differences are generally not too great. The 95% confidence intervals according to our calculations are, however, significantly greater than the non-specified errors given in the literature. In other words the literature seems to suggest a too optimistic picture about the confidence of the reactivity ratios.

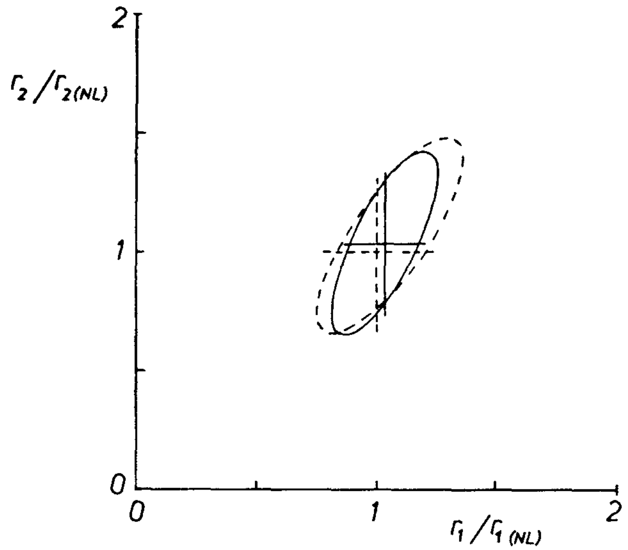

Figure 2. 95% confidence intervals (bars) and 95% joint confidence areas (ovals) of reactivity ratios for System 11 of Table I. Full lines: KT estimation, dotted lines: nonlinear least squares estimation. Data are scaled to the r values of nonlinear estimation.

Using the 95% confidence intervals one can compute parameter $\delta^{\square}$ for each revised system according to the expression

$$\delta^{\square} = \frac{|\Delta r_1 \cdot \Delta r_2|}{r_1 r_2} \qquad (1)$$

This parameter is proportional to the area of the relative error rectangle, and can be applied to characterize the adequacy of measurements. Comparing the $\delta^{\square}$ values listed in Table I with the classifications based on the KT plots, we can state that Class I systems (strict linearity) are characterized by $\delta^{\square} < \sim 0.1$ values. For systems not inconsistent with the line arity hypotheses but having scattered measurement points (Class I(!) systems) greater values were found.

Table I also contains the product $r_1 r_2$ of the newly determined reactivity ratios together with their errors calculated as follows:

$$\Delta\ (r_1 r_2) = r_1 \Delta r_2 + r_2 \Delta r_1 \qquad (2)$$

The mean value of the 14 reactivity ratio products is 1.053. With only two exceptions, the confidence intervals contain the value 1. This means that the assumption of "ideal copolyperization" of butadiene with isoprene under the influence of various anionic stereospecific catalysts, corresponding to

$r_1r_2 = 1$, is consistent with the observed behaviour. On the ground of our results we can state that the classical two-parameter copolymerization model gives a correct description of stereospecific anionic copolymerizations in the majority of cases. The level of error is, according to our experience, relatively moderate and the reproducibility was found better than in cationic systems.

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