

Preparation of polystyrene with low relative molecular mass

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Dedicated to Professor RNDr. J. Gašperík, founder of the Department of Organic Technology and of the Department of Chemical Technology of Plastics and Fibres of the Slovak Technical University on the occasion of the 40th anniversary of their foundation

In the paper the simultaneous influence of temperature and TMTD concentration on the polymerization rate of styrene and $\bar{M}_{r,n}$ of the formed polystyrenes and on the sulfur content in the product was studied. The derived regression equations enable to choose such conditions of the mass polymerization of styrene that polymers with required $\bar{M}_{r,n}$ and sulfur content can be gained. It is possible to control the polymerization rate by suitable temperature. The TMTD concentration does not practically influence the polymerization rate.

В работе исследовалось совместное влияние температуры и концентрации ТМТД на скорость полимеризации стирола, молекулярный вес возникающих полистиролов $\bar{M}_{r,n}$, и содержание серы в продукте. Выведенные регрессионные уравнения позволяют подобрать условия блочной полимеризации стирола так, чтобы была возможность приготовить полимеры с определенным $\bar{M}_{r,n}$ и содержанием серы. Скорость полимеризации можно регулировать подходящей температурой. В изучаемой области концентрация ТМТД на скорость полимеризации практически не влияет.

In several of our papers [1—6] the polymerization course of vinyl monomers initiated by tetramethylthiuram disulfide (TMTD) was described in detail. The investigations have shown that TMTD participates to a significant extent, besides the initiation of polymerization, also in chain transfer reactions and termination reactions. In consequence of the mentioned reactions the formed polymers have a relatively low relative molecular mass and most of the macromolecular chains are at both ends terminated by fragments of TMTD. The papers pointed at the possibility to prepare low-molecular — telechelic polymers by choosing suitable reaction conditions.

It is possible to prepare low-molecular polymers based on vinyl monomers by anionic, cationic or radical polymerization. The anionic polymerization has besides some advantages also considerable disadvantages, and that concerns mainly the requirements for the experimental arrangement and the high purity of the chemicals used. In the cationic polymerization there often occur undesirable secondary reactions, which change the structure and the properties of the formed oligomers [7].

The radical polymerization is very simple and has several advantages in comparison with the ionic polymerization, which is evident from a series of patents claiming the preparation of oligomeric polystyrene. As initiators various substituted peroxides and as regulators of the relative molecular mass disulfides [8—11], mercaptans, and mainly halogenated hydrocarbons [12—15] are used.

In our procedure TMTD is used as initiator and also regulator of the relative molecular mass [16].

Low-molecular polystyrenes with required characteristics can be used with advantage as macromolecular plasticizers, which act at lower temperatures as fillers. The sulfidic reactive end-groups enable to bond chemically the oligomeric polystyrenes on polydiene rubbers.

The processing properties of rubber mixtures in dependence on the amount of oligomeric polystyrene and processing temperature were studied in another of our papers [17]. A positive influence on the processing properties of rubber mixtures at 123 to 142 °C and at a content of 15 to 25 mass % polystyrene on 100 mass % Kralex 010 402 rubber or natural rubber SMR-L was found.

In this paper the results of the study of the influence of temperature and TMTD concentration on the mass polymerization of styrene are summarized with the aim of preparing low-molecular products with bonded sulfidic end-groups.

Experimental

Chemicals

Styrene, commercial grade. The stabilizer was removed by shaking with NaOH solution and water. Then it was dried with CaCl₂ and vacuum rectified in N₂ atmosphere.

Tetramethylthiuram disulfide was purified by threefold precipitation with methanol from a CHCl₃ solution and by crystallization from CHCl₃, *w* (according to elementary analysis) = 99.2 %.

Procedures

The polymerization was carried out in closed ampoules in N₂ atmosphere. TMTD was weighed into ampoules, styrene was added and after bubbling with N₂ and sealing, TMTD

was dissolved by shaking. The conversion was determined after the given time of heating by precipitation of the polymer by methanol. Then it was filtered and dried in vacuum to a constant mass. The polymerization was run up to a conversion of 4.5 to 6.5 %.

The relative molecular mass $\bar{M}_{r,n}$ was determined by vapour osmometry with the Knauer device from three times precipitated samples of polymer.

The sulfur content was determined in three times precipitated samples by a modified method according to Schöniger.

Results

The influence of temperature and TMTD concentration on the polymerization rate of styrene, relative molecular mass $\bar{M}_{r,n}$, and sulfur content in polystyrene was studied by a two-factorial experimental design in five levels [18]. The levels of the factors are in Table 1. The results of the experimental design for the polymerization

Table 1
Levels of factors (independent variables) for the experimental design

X_i	Factor	x_{iu}					I_i
		$-\sqrt{2}$	-1	0	$+1$	$+\sqrt{2}$	
X_1	$\theta/^\circ\text{C}$	55.86	60	70	80	84.14	10
X_2	$\rho(\text{TMTD})/(\text{g}/100 \text{ cm}^3)$	1.172	2.0	4.0	6.0	6.828	2

$$\text{Linear code for the variables: } x_{iu} = \frac{X_{iu} - X_{i0}}{I_i}$$

where X_{iu} = variable in physical units,
 X_{i0} = coordination of the centre of the experiment,
 x_{iu} = code of the variable in the u -level,
 I_i = interval of planning.

rate $v_p - y_1$, relative molecular mass $\bar{M}_{r,n} - y_2$, and sulfur mass fraction $w - y_3$ are summarized in Table 2.

The mean functionality of polystyrenes prepared at various temperatures and TMTD concentrations is $f = 1.623$.

The experimental error for y_1 , y_2 , and y_3 was calculated from five repeated polymerizations (No. 9 to 13) in zero (central) point, that is at 70°C and $\rho(\text{TMTD}) = 4 \text{ g}/100 \text{ cm}^3$ styrene.

It is evident from the evaluation of the mentioned experimental design for the influence of temperature and TMTD concentration that in the studied concentration range polymerization rate does not depend on TMTD concentration. The depend-

Table 2
Results of the experimental design

No.	Code	Temperature		[TMTD]		y_1	y_2	y_3	Functionality
		x_1	$\theta/^\circ\text{C}$	x_2	$\rho/(\text{g}/100 \text{ cm}^3)$	$v_p \cdot 10^5$	$\dot{M}_{r,m}$	$w(\text{S})/\text{mass } \%$	
1	(1)	-1	60	-1	2.0	3.54	11 000	0.92	1.57
2	a	+1	80	-1	2.0	19.73	7 300	1.40	1.59
3	b	-1	60	+1	6.0	4.03	5 400	2.21	1.86
4	ab	+1	80	+1	6.0	19.29	4 300	2.32	1.55
5	-A	-2	55.9	0	4.0	2.51	5 900	1.67	1.54
6	+A	+2	84.1	0	4.0	26.28	4 500	2.34	1.64
7	-B	0	70	-2	1.172	3.83	12 600	0.68	1.34
8	+B	0	70	+2	6.828	4.89	4 100	2.44	1.56
9	0	0	70	0	4.0	5.55	5 500	1.90	1.63
10	0	0	70	0	4.0	5.03	5 800	1.94	1.76
11	0	0	70	0	4.0	4.23	5 700	1.94	1.77
12	0	0	70	0	4.0	3.92	5 600	1.85	1.73
13	0	0	70	0	4.0	4.94	6 100	1.79	1.56

ence of polymerization rate on temperature can, therefore, be expressed by the equation

$$y_1 = \{v_p\} = (4.69 + 8.13x_1 + 5.42x_1^2) \cdot 10^{-5} \quad (1)$$

By means of the F -test it was estimated that the mentioned regression eqn (1) is valid for the experimental area in the level of significance $\alpha = 0.05$.

The estimated independence of the polymerization rate on TMTD concentration is in good agreement with the results of the previous kinetic measurements [1–4]. This is due to the participation of the radicals from TMTD (RS) in the termination reactions.

The study of the influence of temperature and TMTD concentration on the mean relative molecular mass of polystyrenes $\bar{M}_{r,n}$ by means of the mentioned scheme has led to the regression equation in the form

$$y_2 = \bar{M}_{r,n} = 5740 - 847.50x_1 - 2577.63x_2 + 650.00x_1x_2 - 213.75x_1^2 + 1361.25x_2^2 \quad (2)$$

By testing the significance of the coefficients b_0 to b_{22} it was estimated that all are significant in the 5 % significance level. From this follows that in the studied temperature and TMTD concentration range both these factors have a significant influence on $\bar{M}_{r,n}$ of polystyrene. By the F -test it was estimated that the regression eqn (2) is adequate for the experimental area only for the significance level $\alpha = 0.01$.

By means of the canonical form of eqn (2) a contour diagram was made, which is shown in Fig. 1. It is evident that TMTD concentration has the greatest and temperature has a smaller influence on $\bar{M}_{r,n}$ of polystyrenes. With increasing TMTD concentration $\bar{M}_{r,n}$ decreases rapidly, whereas, the temperature remarkably influences $\bar{M}_{r,n}$ only at higher TMTD concentrations ($\rho > 5$ g/100 cm³ styrene). Both factors are mutually influenced.

The estimated experimental error of $\bar{M}_{r,n}$ determination was

$$S(y) = \pm 230$$

The results of sulfur content determination ($w(S)/\text{mass } \%$) in the prepared polystyrene samples in dependence on temperature and TMTD concentration, evaluated by means of the experimental design, have led to the regression equation in the form

$$y_3 = w(S)/\text{mass } \% = 1.8840 + 0.1925x_1 + 0.5875x_2 - 0.0925x_1x_2 + 0.0430x_1^2 - 0.1795x_2^2 \quad (3)$$

The experimental error of $w(S)$ determination was $S(y) = \pm 0.0643$ mass %.

By means of the test of significance it was found that all coefficients in eqn (3) are statistically significant in the 1 and 5 % significance level. Little significant is coefficient b_{12} , but it is impossible to neglect it.

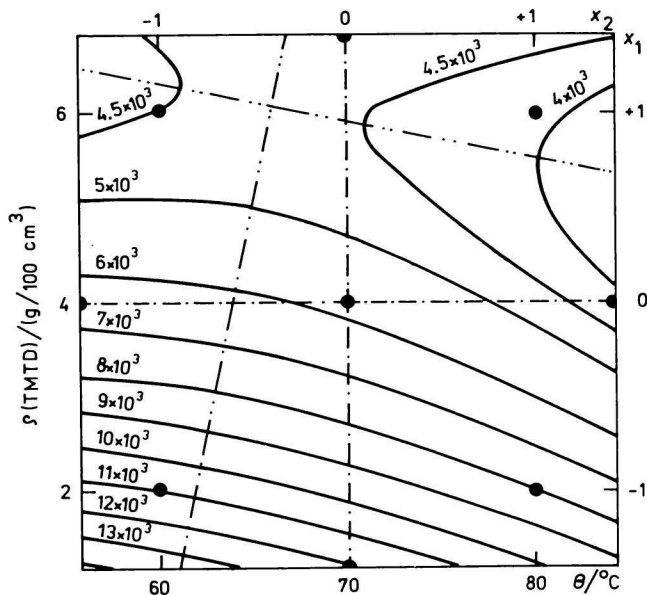


Fig. 1. Contour diagram of the dependence of the relative molecular mass on temperature ($\theta/^\circ\text{C}$) and TMTD concentration ($\rho/(\text{g}/100 \text{ cm}^3 \text{ styrene})$).

By means of the F -test it was found that regression eqn (3) is adequate for the experimental area in the significance level $\alpha = 0.05$.

The contour diagram, made on the basis of the canonical form of eqn (3), is in Fig. 2. It is evident that the sulfur content ($w(\text{S})$) in polystyrenes slightly increases with the polymerization temperature and more rapidly increases with the increasing TMTD concentration.

The experimental results have shown that there is a direct relation between $w(\text{S})$ or the concentration of TMTD fragments and $\bar{M}_{r,n}$ of the synthesized polystyrene samples. From the dependence $w(\text{S}) = f(\bar{M}_{r,n})$ follows that the dependence is hyperbolic and it is possible to express it by the relation

$$\{w(\text{S})\} = b(\bar{M}_{r,n})^{-1} + b_0 \quad (4)$$

In Fig. 3 the dependence $w(\text{S}) = f(\bar{M}_{r,n})^{-1}$ is illustrated. In the figure are also the experimental values of the other samples, which were not comprised in the experimental design and of control samples.

The parameters b and b_0 of eqn (4) were estimated by means of the method of least square means and their values were

$$b = 9954; \quad b_0 = 0.14$$

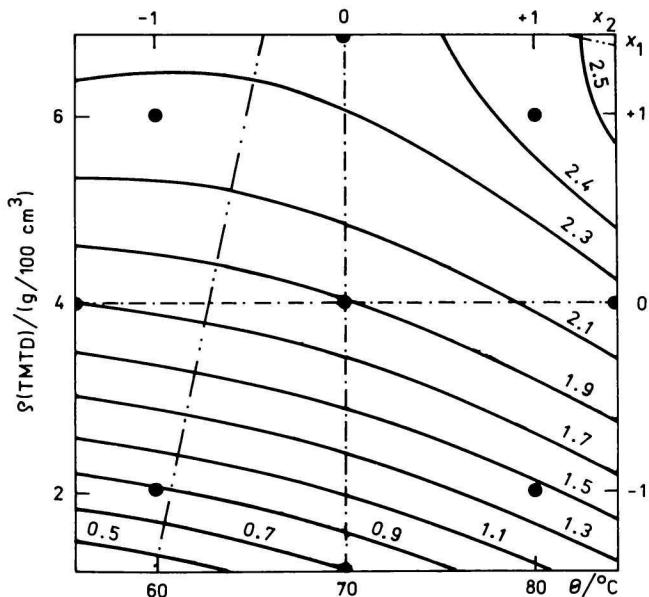


Fig. 2. Contour diagram of the dependence of $w(S)/\text{mass \%}$ on temperature ($\theta/^\circ\text{C}$) and TMTD concentration ($\rho/(\text{g}/100 \text{ cm}^3 \text{ styrene})$).

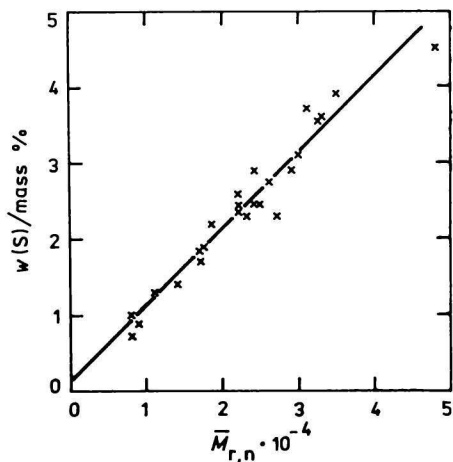


Fig. 3. Dependence of sulfur content ($w/\text{mass \%}$) on $(\bar{M}_{r,n})^{-1}$ of polystyrene samples prepared at various temperatures and TMTD concentrations.

The correlation coefficient was $r = 0.9714$, which indicates a very good linear dependence expressed by eqn (4). It proves simultaneously that in a wide temperature and TMTD concentration range, the prepared polystyrenes have a steady average functionality, calculated from all experimental values mentioned in Fig. 3, $\bar{f}_n = 1.66 \pm 0.16$.

The regression equation stated in the paper enables with good accuracy to determine conditions for the preparation of low-molecular polystyrenes with the desired $\bar{M}_{r,n}$ or the content of sulfidic fragments and to choose the polymerization rate.

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