European Polymer Journal. Vol. 15, pp. 701 to 705
© Pergamon Press Ltd 1979. Printed in Great Britain

0014-3057/79/0701-0701$02.00/0

TERMINATION AND TRANSFER OF THE POLYMER CHAIN TO A MALEIMIDE DERIVATIVE CONTAINING THE AZO GROUP

F. Hrabák and J. Lokaj
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia

(*Received* 21 *June* 1978)

Abstract—The copolymerizations of *N*-(3-dimethylaminophenyl) maleimide (**I**) and 4-(2-chlorophenyl)-azo-3-maleimido-*N*,*N*-dimethylaniline (**II**) with styrene were investigated; the copolymerization parameters of the pairs (**I** + styrene) and (**II** + styrene) and $k_p/k_t^{1/2}$ hr **I** at 50° were determined; chain transfer to the maleimide ring of **I** was proved. The homopolymerization of styrene in the presence of 4-(2-chlorophenyl)azo-succinimide-*N*,*N*-dimethylaniline (**III**) was used to determine the ratio of the rate constant for addition of the polystyrene radical to the azo group in **III** to k_p for styrene.

INTRODUCTION

Comonomers containing the azo group reduce the average degree of polymerization [1] and possess a relatively weak polymerization activity compared with other coloured comonomers [2].

We have reported that unlike **I** [4], 4-arylazo-3-maleimido-*N*,*N*-dimethylanilines [3] do not homopolymerize, although they copolymerize with styrene, methyl methacrylate, acrylonitrile and isobutylene. The copolymerization of **II** with styrene is faster than the homopolymerization of styrene, attaining its maximum rate at 25% mol of **II** in the feed while the limiting viscosity number [η] of the copolymer is lower than that of polystyrene and decreases with increasing concentration of **II** in the feed. Monomer **I** homopolymerizes more rapidly than styrene and is an effective chain transfer agent; the low-molecular weight model for polymer **I**, i.e. *N*-(3-dimethylaminophenyl) succinimide, hardly affects the polymerization rate of styrene and [η] of polystyrene [5].

In order to explain the basic copolymerization characteristics of 4-arylazo-3-maleimido-*N*,*N*-dimethylanilines, we investigated the copolymerization of **I** and **II** with styrene and the effect of **III** on the homopolymerization of styrene.

EXPERIMENTAL

Materials

The formulae and characteristics of *N*-(3-dimethylaminophenyl) maleimide (**I**) [4], 4-(2-chlorophenyl)azo-3-

Table 1. Formulae and characteristics of monomers **I** and **II** and of the model compound **III**

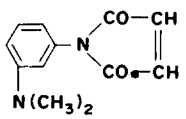
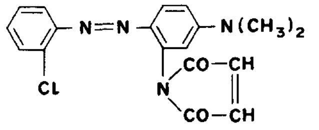
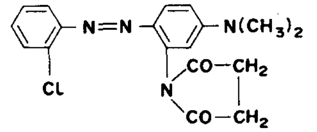
Compound	Formula Mol. wt	M.p. (°)	Calc./Found (%) C	 H	 N
I	 216.25	98–99		[4]	
II	 354.61	150–1		[3]	
III	 356.63	183	60.57 60.43	4.80 4.86	15.71 15.41

Table 2. Copolymerization of I and III with styrene (*st*) in DMF solution at 50°; $\bar{v}$ = average kinetic chain length;

$$n_I = \frac{[I]}{[I] + [st]},\ n_{II} = \frac{[II]}{[II] + [st]};\ n'_I \text{ and } n'_{II}$$

molar fractions of I and II in copolymers; $[I] + [st] = [II] + [st] = 0.67\ \mathrm{mol\ dm^{-3}}$; $[\mathrm{AIBN}] = 3.05\ \mathrm{mmol\ dm^{-3}}$.

n_I n_{II}	$R_p \cdot 10^6$ (mol dm^{-3} sec^{-1})	$\bar{v}$	n'_I n'_{II}	$[\eta]$* (cm^3 g^{-1})
0.0	0.65	113	Polystyrene	14.4
0.0				
0.25	15.36	2670	0.493	41.4
0.25	1.04	181	0.468	7.9
0.30	13.10	2277	0.501	39.0
0.30	0.85	148	0.477	7.3
0.35	10.52	1829	0.514	33.5
0.35	0.76	132	0.481	7.1
0.45	7.36	1279	0.524	29.8
0.45	0.62	108	0.492	
0.50	6.84	1189	0.534	25.2
0.50			0.496	
0.55	5.45	947	0.546	
0.55				
0.60	4.55	791	0.557	
0.60			0.505	
1.00	0.85	148	1.00	6.8
1.00	0.0		—	

* Dimethylformamide, 20°.

maleimido-*N*,*N*-dimethylaniline (**II**) [3] and 4-(2-chlorophenyl)azo-3-succinimido-*N*,*N*-dimethylaniline (**III**) are given in Table 1. **III** was prepared similarly to **II** [3] by coupling *N*-(3-dimethylaminophenyl) succinimide with the diazonium salt of 2-chloroaniline. Styrene, 2,2'-azobis(isobutyronitrile (AIBN), dimethylformamide (DMF) and benzene were purified by the usual methods. [5, 6].

Methods

For study of the copolymerizations of (**I** + styrene) and (**II** + styrene) in DMF, the total concentration of monomers was 0.67 mol dm^{-3}. The mol fractions n_I and n_{II} in the monomer mixtures ranged between 0.25 and 0.60. The AIBN concentration was 3.05 mmol dm^{-3}; the polymerization temperature was 50°; conversions did not exceed 10%. The compositions of copolymers, reprecipitated from chloroform with ethanol, were calculated from nitrogen contents. Monomer reactivity ratios were calculated using the Fineman–Ross method. Values of $[\eta]$ of copolymers were measured in DMF at 20° using an Ubbelohde viscometer.

Chain transfer to **III** in the polymerization of styrene was determined as described earlier [5]. The respective concentrations of styrene and AIBN were 2.16 mol dm^{-3} and 3.05 mmol dm^{-3}. The number average degrees of polymerization, $\bar{P}_n$, were determined in benzene solution with a Hallikainen model 1361 DS4 osmometer.

RESULTS

Copolymerization of I *and* II *with styrene*

Table 2 shows the dependence of the rate of copolymerization of **I** and **II** with styrene and of $[\eta]$ of the resulting copolymers on n_I and n_{II} in the starting feed. The average kinetic chain length ($\bar{v}$) was calculated from Eqn (1)

$$\bar{v} = \frac{R_p}{2k_d f[\mathrm{AIBN}]}, \qquad (1)$$

where k_d at 50° is $2.3 \times 10^{-6}\ \mathrm{sec^{-1}}$ [7] and $f = 0.41$ [5].

At $n_I = 0.25$, the copolymerization is 23 times faster than the homopolymerization of styrene, and $[\eta]$ of the copolymer is about 6 times higher than that of the homopolymer of **I** in DMF. With increase in n_I, both R_p and $[\eta]$ decrease to the values of the homopolymer of **I**.

At $n_{II} = 0.25$, R_p is only little higher (by approx. 40%) than for the homopolymerization of styrene ($n_{II} = 0$). With increase in n_{II}, the copolymerization is slowed down and homopolymerization of **II** is virtually absent; $[\eta]$ of the copolymer (**II** + styrene) is lower than that of polystyrene, varying only little with n_{II}.

The copolymerization parameters of (**I** + styrene) and (**II** + styrene) in DMF at 50° are

$$r_I = k_{II}/k_{Ist} = 0.19, \quad r_{st} = 0.03$$

$$r_{II} = k_{II\,II}/k_{II,st} = 0.04; \quad r'_{st} = 0.05.$$

4-(2-Chlorophenyl)azo-3-succinimido-*N*,*N*-dimethylaniline (**III**) was used as a model for poly(**II**) and

Table 3. Polymerization of styrene in benzene solution in the presence of 4-(2-chlorophenyl)azo-3-succinimido-*N*,*N*-dimethylaniline (**III**) at 50°; [styrene] = 2.16 mol dm^{-3}, [AIBN] = 3.05 mmol dm^{-3}

$\frac{[\mathrm{III}]}{[\mathrm{styrene}]} \cdot 10^3$	$R_p \cdot 10^6$ (mol dm^{-3} sec^{-1})	$\bar{P}_n$	$\bar{v}$*
0	2.73	754	374
2	2.48	640	340
4	2.30	605	315
6	2.13	535	292
8	2.00	517	274

* Calculated according to Eqn (1), with $f = 0.52$ [5].

a study was made of its effect on the polymerization of styrene. Table 3 shows that increasing concentration of III in the mixture causes both R_p and $\overline{P}_n$ to decrease. The experimentally determined $\overline{P}_n$ is approximately twice $\bar{v}$.

DISCUSSION

The rate of copolymerization of **I** + *styrene and calculation of* $k_p/k_t^{1/2}$ *for* **I**.

It follows from the copolymerization parameters for (**I** + styrene) that the rate constant of cross-addition $\sim\dot{\mathrm{I}} + \mathrm{st}$ is 5 times, and that of cross-addition $\sim\dot{st} + \mathbf{I}$ approximately 30 times higher than the rate constant of homoaddition $\sim\dot{\mathbf{I}} + \mathbf{I}$ or $\sim\dot{st} + st$. Since r_{st} (0.03) approaches zero, the rate of copolymerization (I + styrene) may be expressed [8] in terms of the reduced copolymerization Eqn (2),

$$R_p = -\frac{\mathrm{d}([\mathrm{I}] + [st])}{\mathrm{d}t} = \left([\mathrm{I}] + \frac{2[st]}{r_\mathrm{I}}\right)R_i^{1/2}A_\mathrm{I} \quad (2)$$

in which $R_i = 2\,k_d f[\mathrm{AIBN}]$ and $A_\mathrm{I} = k_{p(\mathrm{I})}/k_{t(\mathrm{I})}^{1/2}$, $k_{p(\mathrm{I})}$ and $k_{t(\mathrm{I})}$ being the rate constants of propagation and bimolecular termination in the homopolymerization of **I**. After expressing the concentrations [**I**] and [st] by means of the mol fraction n_I, and calculating $R_i^{1/2}$ and r_I (Table 2 and "Results"), Eqn (2) becomes:

$$2066.12\,R_p = (1.105 - n_\mathrm{I})A_\mathrm{I} \quad (3)$$

From this equation Fig. 1 can be deduced. The value $\log A_\mathrm{I} = -1.35$ from Fig. 1 corresponds to the ratio of constants $k_{p(\mathrm{I})}/k_{t(\mathrm{I})}^{1/2} = A_\mathrm{I} = 0.045$ dm$^{3/2}$ mol$^{-1/2}$ sec$^{-1/2}$. A_I was also calculated from data on the homopolymerization of **I** in DMF [5] using Deb's equation. Two independent constructions of hyperbolic dependences and their solutions [5] yielded for A_I 0.035 and 0.06 dm$^{3/2}$ mol$^{-1/2}$ sec$^{-1/2}$. Consequently, $A_\mathrm{I} = 0.045$ dm$^{3/2}$ mol$^{-1/2}$ sec$^{-1/2}$ obtained from Fig. 1 is approximately the mean of the former two values; it is higher than that for styrene [7] ($A_{st} = 0.015$) and lower than that for *N*-(3-dimethylamino-6-methylphenyl) maleimide [5] ($A = 0.094$ dm$^{3/2}$ mol$^{-1/2}$ sec$^{-1/2}$).

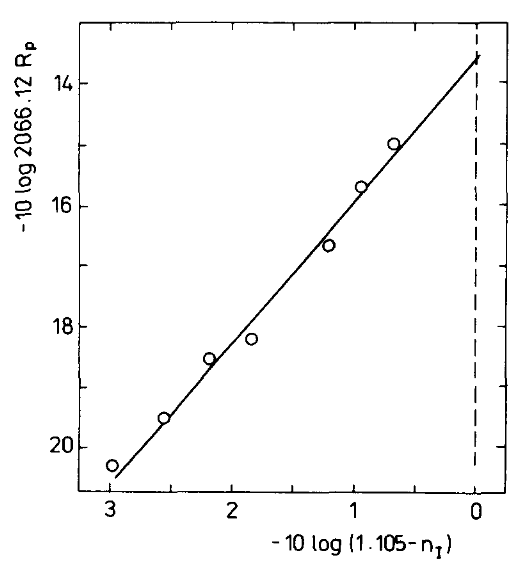


Fig. 1. Graphical determination of $k_{p(\mathrm{I})}/k_{t(\mathrm{I})}^{1/2}$ using Eqn (3).

Transfer in the copolymerization of (**I** + *styrene*) *to monomer* **I** and DMF

Data in Table 2 show that the ratio of values of $\bar{v}^{0.7}$ at $n_\mathrm{I} = 0.25$ and $n_\mathrm{I} = 0$ (a = 0.7 is the most frequent exponent in the Eqn $[\eta] = k\overline{P}_\eta^a$) is 9.1, while the ratio of $[\eta]$ values of the copolymer and polystyrene is 2.9. The large difference between these ratios indicates transfer of the polymer radical during copolymerization. Monomer **I** is an effective chain transfer agent in the homopolymerization of **I** [5] and probably participates in this transfer. This view may be confirmed by the following analysis:

By analogy with the homopolymerization of **I**, assume that it is predominantly the radical $\sim\dot{\mathbf{I}}$ which transfers to monomer **I** while the radical $\sim\dot{st}$ transfers negligibly. Taking into account the order of homopolymerization of styrene or **I** with respect to AIBN in DMF (≈ 0.5), combination of the copolymer radicals may be regarded as the dominant termination [5]. The growth, termination and transfer of radicals may then be represented by scheme 1.

Scheme 1

(a) $\sim\dot{st} + \mathbf{I} \longrightarrow \sim\dot{\mathbf{I}}$ cross-addition
(b) $\sim\dot{\mathbf{I}} + st \longrightarrow \sim\dot{st}$ cross-addition
(c) $\sim\dot{\mathbf{I}} + \mathbf{I} \longrightarrow \sim\dot{\mathbf{I}}$ homo-addition
(d) $\sim\dot{\mathbf{I}} + \mathbf{I} \longrightarrow$ polymer $+ \dot{\mathbf{I}}_{tr}$ transfer to **I**
(e) $\sim\dot{st}$ (or $\sim\dot{\mathbf{I}}$)
$+$ DMF $\longrightarrow$ polymer $+ \mathrm{D\dot{M}F}_{tr}$ transfer to DMF
(f) $\dot{\mathbf{I}}_{tr}$ (or $\mathrm{D\dot{M}F}_{tr}$) $+ st \longrightarrow \sim\dot{st}$ re-initiation
(g) $\dot{\mathbf{I}}_{tr}$ (or $\mathrm{D\dot{M}F}_{tr}$) $+ \mathbf{I} \longrightarrow \sim\dot{\mathbf{I}}$ re-initiation

Using the copolymerization parameter $r_\mathrm{I} = k_{\mathrm{II}}/k_{\mathrm{I}_{st}} = 0.19$ and the relative transfer constant [5] of polymer radical **I** to monomer **I** ($k_{\mathrm{II}(tr)}/k_{\mathrm{II}} \approx 0.07$), one obtains

$$\frac{k_{\mathrm{I}st}[\dot{\mathrm{I}}][st]}{k_{\mathrm{II}(tr)}[\dot{\mathrm{I}}][\mathrm{I}]} = \frac{k_{\mathrm{I}st}[st]}{0.07k_{\mathrm{II}}[\mathrm{I}]} = \frac{75[st]}{[\mathrm{I}]}.$$

In the case of alternating structural units in polymer chains, the number of elementary reactions (b) is approximately the same as the number of elementary reactions (a). Consequently, the addition of 2 × 75 $[st]/[\mathrm{I}]$ structural units corresponds to one transfer process (d). If the transfer of copolymer radicals to dimethylformamide ($[\mathrm{DMF}] \doteq 12$ mol dm^{-3}) is approximately the same as in the homopolymerization of styrene [5] in DMF, $[C_{\mathrm{DMF}}\mathrm{DMF}]$: $([st] + [\mathrm{I}]) = 15.8 \times 10^{-4}$.

In accordance with the described main ways of transformation of the polymer radical into a macromolecule

$$\frac{1}{\overline{P}_n} = \frac{1}{2\bar{v}} + \frac{[\mathrm{I}]}{150[st]} + 15.8 \times 10^{-4}. \quad (4)$$

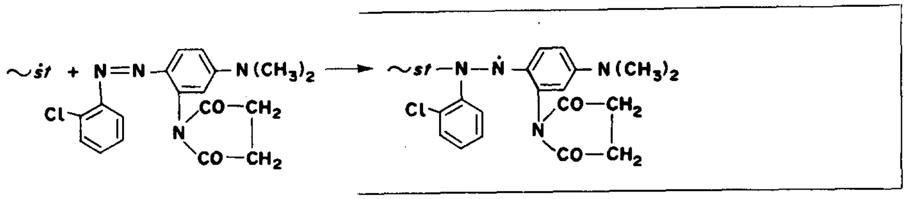
Equation (4) and data in Table 2 were used to calculate $\overline{P}_n$. For $n_\mathrm{I} = 0.25$, 0.30, 0.35, 0.45 and 0.50, the respective values of $\overline{P}_n$ are 251, 215, 184, 135 and 115. Since the composition of the respective copolymers varies insignificantly, the calculated values of $\bar{P}_n$ were recalculated to $[\eta]$ by means of Eqn (9):

$$[\eta] = k\bar{P}_n^a\left(1 + \frac{1+a}{2c}\right)^a. \qquad (5)$$

Here, $a = 0.7$ is the most usual exponent in the Eqn $[\eta] = k\bar{P}_\eta^a$ and c denotes the number of polymer radicals which form the macromolecule; $c = 1.0$ was chosen, because the first term on the righthand side of the Eqn (4) is approximately only one twentieth of the sum of terms on the righthand side of Eqn (4). The constant k was calculated at one concentration of **I** by substituting the respective experimentally determined $[\eta]$ into Eqn (5). Using k thus determined (at $n_{\rm I} = 0.25$, it is 0.5627), $[\eta] = 37.8$, 33.3, 26.8 and 24.8; 24.0 cm^3 g^{-1} was calculated for $n_{\rm I} = 0.30$, 0.35, 0.45 and 0.50. The satisfactory agreement with the measured $[\eta]$ (in Table 2) indicates the increasing participation of chain transfer of $\sim\dot{\rm I}$ to monomer **I** with increasing concentration of **I** and the transfer of all polymer chains to solvent (DMF). If transfer to solvent is neglected, the calculated values of $[\eta]$ for $n_{\rm I} = 0.30$, 0.35, 0.45 and 0.50 are respectively 34.9, 29.8, 22.3 and 19.4 cm^3 g^{-1}, thus differing considerably from experimental values. It has been shown earlier [5] that *N*-(3-dimethylaminophenyl) succinimide hardly affects the rate of polymerization of styrene and the degree of polymerization. Hence it may be inferred that transfer of the copolymer chain occurs to the maleimide ring of monomer **I**.

Addition of the polystyrene radical to the azo group of **III** *and copolymerization* (**II** + styrene)

The observed interaction of polystyrene radicals with the 2-chlorophenylazo group of monomer **II** was studied using 4-(2-chlorophenyl)azo-3-succinimido-*N*,*N*-dimethylaniline (**III**). The decrease in R_p and $\bar{P}_n$ with increasing concentration of **III** in the starting polymerization mixtures (Table 2) indicates retardation [10] in which chain propagation ceases after addition of a molecule of the retarder. At the same time, the ratio of determined $\bar{P}_n$ to calculated $\bar{\nu}$ (Table 3) suggests that combination of polymer radicals predominates. Since some azoarenes [11] and azoalkanes [12] may add aryl or alkyl radicals with formation of hydrazyl radicals, one may similarly assume addition of the polystyrene radical to the azo group of **III**:



The likely mechanism of the polymerization of styrene in the presence of **III** is shown in scheme 2.

Scheme 2

(a′) $\mathrm{AIBN} \xrightarrow{k_d} 2\mathrm{R}$

(b′) $\mathrm{R} + st \xrightarrow{k_i} \sim\dot{s}t$

(c′) $\sim\dot{s}t + st \xrightarrow{k_p} \sim\dot{s}t$

(d′) $\sim\dot{s}t + \mathrm{N{=}N} \xrightarrow{k_{tr}} \sim\mathrm{N{-}\dot{N}}$

(e′) $\sim\dot{s}t + \sim\dot{s}t \xrightarrow{k_t} \text{polymer}$

(f′) $\sim\dot{s}t + \sim\mathrm{N{-}\dot{N}} \xrightarrow{k_t'} \text{polymer}$

(g′) $\sim\mathrm{N{-}\dot{N}} + st \longrightarrow \sim\dot{s}t$

(h′) $\sim\mathrm{N{-}\dot{N}} + \sim\mathrm{N{-}\dot{N}} \longrightarrow \text{polymer.}$

If the latter two reactions are neglected, consideration of the remaining reactions yields Eqn (6).

$$\frac{k_d f[\mathrm{AIBN}]}{R_p} - \frac{k_t R_p}{2k_p^2[st]^2} = \frac{k_{tr}[\mathrm{N{=}N}]}{k_p[st]}. \qquad (6)$$

If the polymerization rate of styrene without the azo compound $(R_{p,0})^2$ is substituted for $2k_p^2k_t^{-1}k_d f[\mathrm{AIBN}]$ $[st]^2$, Eqn (6) becomes Eqn (7)

$$\frac{R_{p,0}^2 - R_p^2}{R_p[st]^2} = \frac{2k_pk_{tr}[\mathrm{N{=}N}]}{k_t[st]}. \qquad (7)$$

Substitution of data from Table 3 into Eqn (7) led to a linear dependence (Fig. 2) with slope $2k_pk_{tr}/k_t = 4.76 . 10^{-5}$ dm^3 mol^{-1} sec^{-1}. The slope and the known [7] value $k^2p_p^2/k_t$ for styrene at 50° ($= 2.31 \times 10^{-4}$ dm^3 mol^{-1} sec^{-1}) led to $k_{tr}/k_p = 0.10$.

It is likely that, also in the homopolymerization of **II**, polymer radicals $\sim\dot{\mathbf{I}}\mathbf{I}$ (and probably primary radicals from the initiator) are added to the azo group of monomer **II**. If at the same time the ratio of the rate constants of reactions of radical $\sim\dot{\mathbf{I}}\mathbf{I}$ with the azo group of **II** and with the maleimide ring of **II** is close to the value of k_{tr}/k_p given above, the number of molecules of polymerized **II** corresponds to approximately ten times the number of molecules of decomposed AIBN, if $f \approx 0.5$.

For copolymerization of **II** with styrene, it may be assumed that, along with the addition of the copolymer radical $\sim\dot{s}t$, the copolymer radical $\sim\dot{\mathbf{I}}\mathbf{I}$ also adds to the azo group **II**. In spite of this, however, at $n_{\rm II}$ from 0.25 to 0.35 (Table 2) both R_p and $\bar{\nu}$ are higher than for the homopolymerization of styrene. This is obviously a consequence of an approximately 20-fold increase in the rate constants of cross-addition compared with those of the homo-addition of comonomers in the copolymerization. On the other hand, values of $[\eta]$ of copolymers at $n_{\rm II}$ from 0.25 to 0.35 are lower than for the homopolymer of styrene, indicating considerable transfer of the copolymer chain to the maleimide ring of monomer **II**. At $n_{\rm II} = 0.45$, R_p is lower than for homopolymerization of styrene. With further increase in $n_{\rm II}$, the probability of addition of the copolymer radical to the azo group of

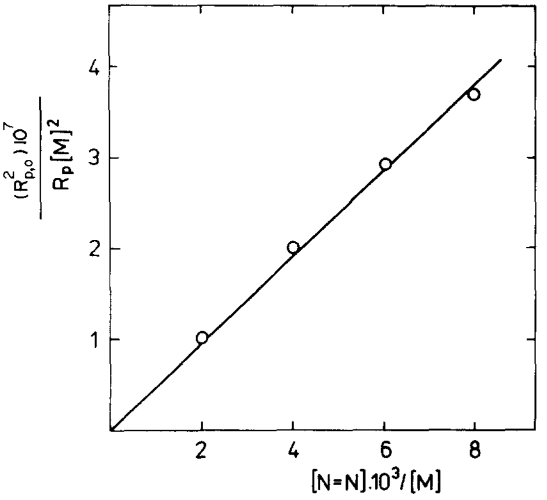


Fig. 2. Graphical determination of k_pk_{tr}/k_t using Eqn (7).

II increases and R_p decreases, becoming virtually zero for the homopolymerization of II.

The addition of primary butyronitrile radicals to the azo group of II probably reduces the initiation efficiency (f) in the copolymerization (**II** + styrene). If at the same time the ratio of rate constants for reactions of $(CH_3)_2CCN$ with the azo group of **II** and with the C=C bonds of both components is close to $k_{tr}/k_p = 0.1$, f at $n_{II} = 0.50$ differs from f at $n_{II} = 0.0$ ($f = 0.41$) by $fn_{II}k_{tr}/k_p = 0.02$. It is obvious that the calculated deviation does not require any considerable changes in conclusions derived from the copolymerization of **II** with styrene assuming constant f.

REFERENCES

1. H. Kamogawa, M. Kato and H. Sugiyama, *J. Polym. Sci. A1* **6**, 2967 (1968).
2. T. Konstantinova, C. Konstantinov and A. Draganov, *Angew. Makromolek. Chem.* **50**, 1 (1976).
3. J. Lokaj and F. Hrabák, *Angew. Makromolek. Chem.* **67**, 1 (1978).
4. J. Lokaj, V. Hynková, Svobodová and F. Hrabák, *Collect. Czech. Chem. Commun.* **42**, 1830 (1977).
5. J. Lokaj and F. Hrabák, *Eur. Polym. J.* **14**, 1039 (1978).
6. F. Hrabák and L. Jirešová, *Collect, Czech. Chem. Commun.* **26**, 1283 (1961).
7. Kh. S. Bagdasarjan, Teoria radikalnoj polimerizacii, *Izd. Nauka*, Moscow 1966.
8. C. Walling, *J. Am. chem. Soc.* **71**, 1930 (1949).
9. G. Henrici-Olivé and S. Olivé, *Z. phys. Chem.* **19**, 125 (1959).
10. H. W. Melwille and W. F. Watson, *Trans. Faraday Soc.* **44**, 886 (1948).
11. L. Benati, G. Placucci, P. Spagnolo, A. Tundo and G. Zanardi, *J. Chem. Soc., Perkin Trans. I*, 1684, (1977).
12. O. P. Strausz, R. E. Berkley and H. E. Gunning, *Can. J. Chem.* **47**, 3470 (1969).