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### Intramolecular Charge Transfer Complexes. 3. Another Approach to the Charge Transfer Copolymerization Model

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## **Intramolecular Charge Transfer Complexes.**

### **3. Another Approach to the Charge Transfer Copolymerization Model**

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#### **ABSTRACT**

The usual copolymerization equation obtained for the terminal charge transfer model by Seiner and Litt is discussed. A new definition, valuable especially for K-values higher than 0.03 and for systems having low probabilities of the homopropagation reactions, is proposed for the reactivity ratios. The higher generality of the new equation is demonstrated on two systems. Two FORTRAN programs for nonlinear estimation with least-square error of the parameters are presented and discussed.

#### **GENERAL CONSIDERATIONS**

Intramolecular charge transfer complexes (CTC) can be obtained by copolymerization of monomers having electrono-donor groups with monomers having electrono-acceptor groups. The copolymers obtained will have an intramolecular CTC character, the intramolecular charge transfer interactions depending on composition, sequence distribution, configuration, and conformation [1]. In order to find the dependence of physical properties on the microstructure of such CTC, it is very important to determine the copolymerization mechanism and the kinetic parameters which decide the copolymer composition and microstructure.

Seiner and Litt [2] proposed a copolymerization model which implies "weak" intermonomeric CTC. The two monomers give a complex:

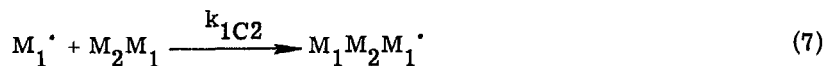
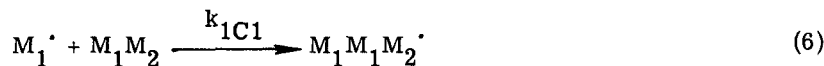


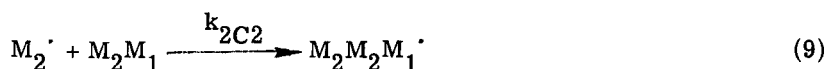
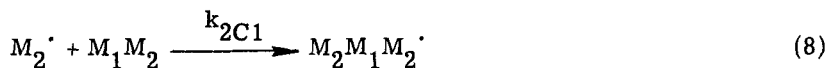
which acts as a separate entity in copolymerization. The existence of CTC and its participation in copolymerization is demonstrated by differences in copolymer composition when changing the total monomer concentration in the copolymerization solvent, or when changing the solvent (using a donor-type, acceptor-type, or an inert solvent).

Recently, Kelen and Tüdös [3] proposed an equation to determine reactivity ratio values and to verify the validity of the terminal model in copolymerization. For all systems analyzed by Seiner and Litt, the Kelen-Tüdös plot is a curve and not a straight line. Therefore, the need for another copolymerization model implying intermonomeric CTC can be tested simpler than usual without the necessity to work at different concentrations in different solvents. The testing procedure is as follows: to point out the intermonomeric CTC through a spectral (UV [4], NMR [5-7]) method; and to plot the Kelen-Tüdös equation, which is a curve and not a straight line.

#### EQUATION PROPOSED BY SEINER AND LITT

The most general case for the propagation reactions was taken into account by Seiner and Litt [2]:





Writing, according to these equations, the probabilities of obtaining  $ij$  sequences from  $i$ -ended macroradicals ( $P_{ij}$ ) and using the steady-state condition ( $M_1 \cdot \rightarrow M_2 \cdot = M_2 \cdot \rightarrow M_1 \cdot$ ) and the copolymerization equation  $y = P_{21}/P_{12}$  (where  $y = d[M_1]/d[M_2]$ ), Seiner and Litt gave the general form of the copolymerization equation implying intermonomeric CTC:

$$y = \frac{1 + \left( \frac{r_{21}}{r_{2C2}} + \frac{r_{21}}{r_{2C1}} \right) \frac{[C]}{[M_1]} + \frac{r_{12}[C]}{r_{1C2}[M_2]} \frac{1 + \frac{r_{21}[C]}{r_{2C2}[M_1]}}{1 + \frac{r_{12}[C]}{r_{1C1}[M_2]}}}{r_{21} \frac{[M_2]}{[M_1]} + 1 + \left( \frac{2r_{21}}{r_{2C2}} + \frac{r_{21}}{r_{2C1}} \right) \frac{[C]}{[M_1]} + \frac{r_{12}[C]}{r_{1C2}[M_2]} \frac{1 + \frac{r_{21}[C]}{r_{2C2}[M_1]}}{1 + \frac{r_{12}[C]}{r_{1C1}[M_2]}}}$$

$$= \frac{1 + \left( \frac{r_{12}}{r_{1C1}} + \frac{r_{12}}{r_{1C2}} \right) \frac{[C]}{[M_2]} + \frac{r_{21}[C]}{r_{2C1}[M_1]} \frac{1 + \frac{r_{12}[C]}{r_{1C1}[M_2]}}{1 + \frac{r_{21}[C]}{r_{2C2}[M_1]}}}{r_{12} \frac{[M_1]}{[M_2]} + 1 + \left( \frac{2r_{12}}{r_{1C1}} + \frac{r_{12}}{r_{1C2}} \right) \frac{[C]}{[M_2]} + \frac{r_{21}[C]}{r_{2C1}[M_1]} \frac{1 + \frac{r_{12}[C]}{r_{1C1}[M_2]}}{1 + \frac{r_{21}[C]}{r_{2C2}[M_1]}}}$$

$$(10)$$

where

$$[C] = [M_1M_2] = \frac{1}{2}([M_1]_0 + [M_2]_0 + 1/K) - \frac{1}{2}\{([M_1]_0 - [M_2]_0)^2 + (2/K)([M_1]_0 + [M_2]_0) + (1/K^2)\}^{1/2} \quad (11)$$

$$r_{12} = k_{11}/k_{12}; \quad r_{1C1} = k_{11}/k_{1C1}; \quad r_{1C2} = k_{11}/k_{1C2} \quad (12)$$

$$r_{21} = k_{22}/k_{21}; \quad r_{2C1} = k_{22}/k_{2C1}; \quad r_{2C2} = k_{22}/k_{2C2} \quad (13)$$

#### PARTICULAR CASES. KARAD AND SCHNEIDER EQUATION

(a) When  $K < 0.03$ , the intermonomer CTC concentration can be calculated by the relation  $[C] = K[M_1]_0[M_2]_0$ . Equation (10) was not significantly simplified.

(b) The case  $k_{22} = 0$  (one of comonomers does not homopolymerize) was analyzed in detail by Seiner and Litt and Karad and Schneider [8]. Supposing also that  $k_{2C2} = 0$ , Eq. (10) was reduced to:

$$y - 1 = \frac{r_{12}([M_1]/[M_2]) + r_{12}[C]/r_{1C1}[M_2]}{1 + r_{12}[C]/r_{1C1}[M_2] + r_3([C]/[M_1])(1 + r_{12}[C]/r_{1C1}[M_2])} \quad (14)$$

where  $r_3 = r_{21}/r_{2C1} = k_{2C1}/k_{21}$ ;  $r_{1C} = k_{11}/k_{1C}$ ;  $k_{1C} = k_{1C1} + k_{1C2}$ . Because the contribution of the term  $r_3[C]/[M_1]$  can be neglected [2], Eq. (14) is particularized in a linear form, from which the reactivity ratio values  $r_{12}$ ,  $r_{1C1}$ , and  $r_{1C2}$  can be obtained:

$$y - 1 = \frac{r_{1C}}{r_{1C1}} + r_{1C} \left( \frac{[M_1]}{[C]} - \frac{y - 1}{r_{12}} \frac{[M_2]}{[C]} \right) \quad (15)$$

The  $r_3$ -value can be obtained from a rearrangement of Eq. (14), and it has been found to be zero for the system styrene-difumaronitrile [8]. In fact, replacing  $k_{22} = 0$  in Eq. (10) without the need of  $k_{2C2} = 0$ , one obtains Eq. (15) directly.

These equations, together with other linearized forms, were applied

to the systems styrene- $\beta$ -cyanoacroleine, methyl acrylate-diphenyl-ethylene, vinyl acetate-dichlorotetrafluoroacetone, vinyl acetate-hexafluoroacetone, vinyl acetate-tetrachlorocyclopropene, styrene-tetrachlorocyclopropene [2], and styrene-difumaronitrile [8].

Pittman and Rounsefell [9] wrote three FORTRAN programs for nonlinear estimation with minimum square error of the independent parameters in Eq. (10). Because the authors did not find sufficient composition-conversion data in the literature, they used imaginary systems.

### LIMITS OF EXISTENT EQUATIONS

Radical copolymerization of picryl methacrylate ( $M_2$ ) (monomer which does not homopolymerize,  $k_{22} = 0$  [10]) with such different electrono-donor monomers ( $M_1$ ) as N-(2-hydroxyethyl) carbazoyl methacrylate [1], N-ethyl(2-hydroxymethyl) carbazoyl methacrylate,  $\alpha$ -(2-fluorenyl) ethyl methacrylate [11], N-(2-hydroxyethyl) carbazoyl acrylate [12], and 2-naphthyl methacrylate [13] generates two types of copolymerization diagrams (Fig. 1):

- A. The picryl methacrylate structural units in the copolymer are lower than 35-40% for every initial composition domain.
- B. The content of picryl methacrylate in copolymers is relatively high (but does not surpass 50%), even at low feed ratios.

A-type systems can be readily analyzed by Eq. (15), and the reactivity ratio values for  $M_1$ -ended macroradicals are obtained.

B-type systems, generally having comparable K-values with A-type systems, either generate negative values of reactivity ratios by Eq. (15) or do not permit a straight line to be obtained. The explanation for this may be the relatively low homopolymerization tendency of  $M_1$  monomer and/or  $k_{2C2} \neq 0$ .

If  $k_{22} = 0$  and  $k_{11}$  is very close to zero, as the case seems to be for B-type systems, then Eq. (10) and their derivatives become inoperative because all reactivity ratio values are null (Eq. 13) or close to zero (Eq. 12).

The reactivity ratio definition (Eqs. 12 and 13) restricts the applicability of Eq. (10) and its derivatives to systems having a homopropagation reaction comparable with cross-addition or complex addition. Otherwise, in the case  $k_{22} = 0$ , the only case where Eq. (10) has been applied, there is no information on the  $M_2$ -ended macroradical behavior because  $r_{21}$ ,  $r_{2C1}$ , and  $r_{2C2} = 0$ . Moreover, Karad and Schneider demonstrated on the analyzed system that  $k_{22} = 0$ ,  $k_{2C2} = 0$ ,

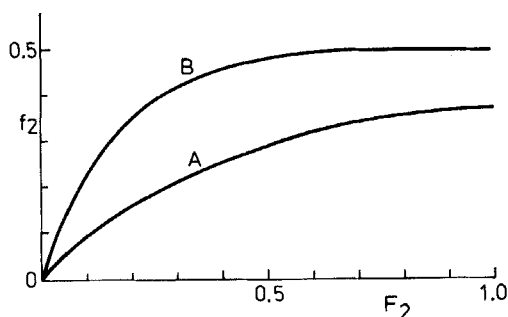


FIG. 1. Copolymerization diagrams (molar fraction of  $M_2$  in copolymer against molar fraction of  $M_2$  in monomer feed) for the two types of systems.

and  $k_{2C1} = 0$  ( $r_3 = 0!$ ), but this means that  $M_2$  does not participate in copolymerization, which is absurd.

The nonsense arises from the  $r_3$  definition, dividing the numerator and the denominator by zero:

$$r_3 = \frac{r_{21}}{r_{2C1}} = \frac{k_{22}/k_{21}}{k_{22}/k_{2C1}} = \frac{k_{2C1}}{k_{21}}, \quad \text{but } k_{22} = 0$$

#### EQUATION PROPOSED AS MODEL FOR CHARGE TRANSFER COPOLYMERIZATION

Especially in B-type systems, but valid for all copolymerization systems having relatively high CTC concentrations ( $K > 0.03$ ), a definition is proposed for the reactivity ratios

$$\alpha_{11} = k_{1C1}/k_{12}; \quad \alpha_{12} = k_{1C2}/k_{12}; \quad \alpha_{1C} = k_{1C}/k_{12};$$

$$r_{12} = k_{11}/k_{12} \quad (16)$$

$$\alpha_{21} = k_{2C1}/k_{21}; \quad \alpha_{22} = k_{2C2}/k_{21}; \quad \alpha_{2C} = k_{2C}/k_{21};$$

$$r_{21} = k_{22}/k_{21} \quad (17)$$

The main term in these equations is the CTC addition rate constant. Through sequence probabilities, one obtains the general equation

$$y = \frac{1 + r_{12} \frac{[M_1]}{[M_2]} + K[C] (\alpha_{11}\alpha_{2C} + \alpha_{22}\alpha_{1C}) + \alpha_{2C} \frac{[C]}{[M_1]} + (\alpha_{11} + \alpha_{1C} + \alpha_{22}r_{12}) \frac{[C]}{[M_2]}}{1 + r_{21} \frac{[M_2]}{[M_1]} + K[C] (\alpha_{11}\alpha_{2C} + \alpha_{22}\alpha_{1C}) + \alpha_{2C} \frac{[C]}{[M_1]} + (\alpha_{22} + \alpha_{1C} + \alpha_{11}r_{21}) \frac{[C]}{[M_2]}} \quad (18)$$

If all  $k_{iCj} = 0$ , then Eq. (18) is reduced to the classical form of the terminal model copolymerization equation, as does Eq. (10). The particular case  $k_{22} = 0$  and  $k_{2C2} = 0$  gives the equation

$$y - 1 = \frac{\alpha_{11}}{\alpha_{1C}} + \frac{r_{12}}{\alpha_{1C}} \left\{ \frac{[M_1]}{[C]} - \frac{y - 1}{r_{12}} \left( \frac{[M_2]}{[C]} + \alpha_{21} \frac{[M_2]}{[M_1]} + \alpha_{11}\alpha_{21} \frac{[C]}{[M_1]} \right) \right\} \quad (19)$$

Equation (19) is identical to Eq. (15) only if  $\alpha_{21} = 0$ , i.e.,  $k_{2C1} = 0$ .

This is impossible, as demonstrated in the preceding section.

Therefore, Eqs. (18) and (19) describe more precisely the mechanism of charge transfer copolymerization.

### COMPUTER PROGRAMS FOR REACTIVITY RATIOS DETERMINATION

Program ESTIM generates the values  $\alpha_{11}$ ,  $\alpha_{12}$ ,  $\alpha_{21}$ ,  $\alpha_{22}$ ,  $r_{12}$ , and  $r_{21}$ , starting from the experimental data ( $[M_1]$ ,  $[M_2]$ ,  $[C]$ ,  $y$ ) and from an initial estimation of the parameters according to Marquardt's algorithm for least-squares error estimation of nonlinear parameters [14]. In order to avoid false local extrema, different sets of starting parameters have been used. The best results are obtained when some parameters can be approximated by Eq. (15), the parameters  $\alpha_{21}$  and  $\alpha_{22}$  being completely unknown. The program does not constrain the parameters to be positive, so that the results containing negative values are considered false local minima for the mean square error. The precision of parameter determination is imposed by the copolymerization experimental error. In order to obtain better precision, an attempt was made to determine the parameters in two steps by using different values for the factor  $\nu$  (which modified the value of the multiplier  $\lambda$  from one iteration to another). In the first step the  $\nu = 10$



value was chosen, then the iterations were restarted for  $\nu = 2$ , using as initial values the result obtained in the former step. In this case the process did not rapidly converge, but an improved precision was obtained (about 30%).

In conclusion, the estimation of all parameters is more difficult to perform starting from any conditions; good results are obtained in the case when 3 or 4 parameters can be predetermined from Eq. (15) or by other means, the program having to find the values of the other 2 or 3 parameters.

Program VERIF computes  $y$  from Eq. (18) and writes the values calculated from the experimental points together with the values of  $y$  experimentally determined to be compared. By using this program it is possible to avoid the choice of a parameter set which, although it generates a small mean square error, can give systematic deviations in the copolymerization diagram.

The programs were written in FORTRAN and run on a FELIX C-32 computer.

#### SYSTEMS ANALYZED BY THE PROPOSED EQUATION

(a) A B-type copolymerization system having the constants  $K = 1$ ,  $\alpha_{11} = 1$ ,  $\alpha_{12} = 5$ ,  $\alpha_{21} = 3$ ,  $\alpha_{22} = 0$ ,  $r_{12} = 0.5$ , and  $r_{21} = 0$  generates the copolymerization diagram given in Fig. 2. This system belongs to the most particular case:  $k_{22} = 0$  and  $k_{2C2} = 0$ . Equation (15) for this system gives the plot of Fig. 3. As can be seen, the points lie on a curve (or on two intersecting lines) and not on a straight line. The Gauss linearization of the points gives the reactivity ratios listed in Table 1. From Table 1 it is clear that the approximation  $\alpha_{21} = 0$

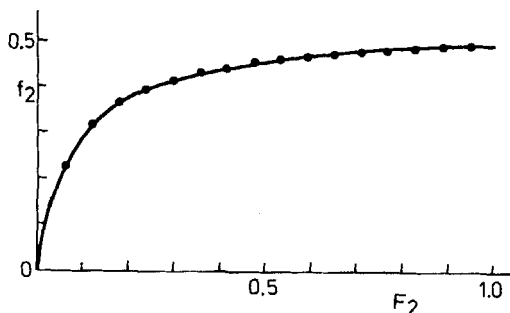


Fig. 2. Copolymerization diagram of the imaginary system.

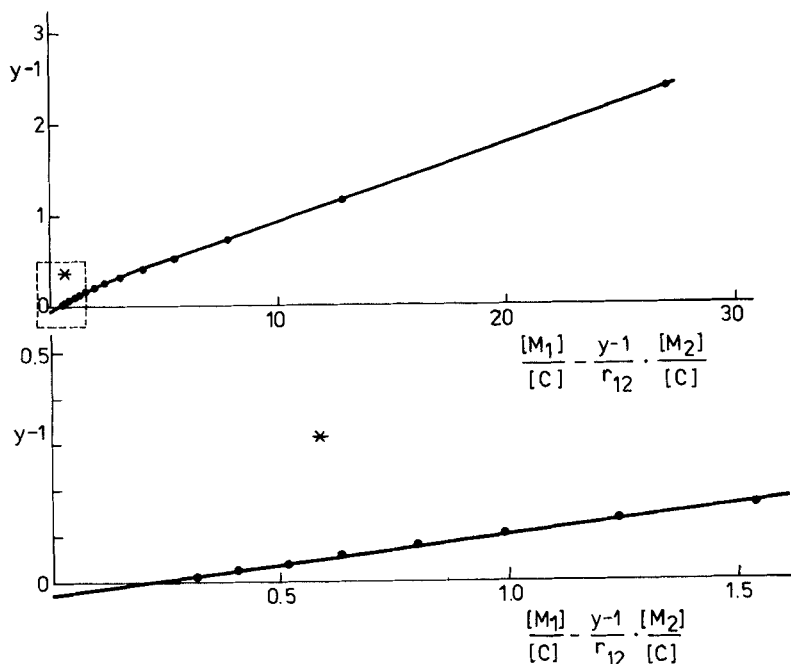


FIG. 3. Reactivity ratios determination by Eq. (15) for the imaginary system.

(implicitly done by Eq. 15) leads to erroneous results. The most affected is  $r_{1C1}$ . Equation (15) suggests that  $M_1$  homopropagation is four times more probable than CTC addition on the same side, but in reality the CTC addition is two times more probable than  $M_1$  homopropagation.

(b) Copolymerization of styrene and difumaronitrile in acetone, analyzed by Karad and Schneider [8], was used as a test for our equation. Although K-value was determined in  $CCl_4$ , and it must be different in an electrono-acceptor solvent (acetone) [7], the values given by the authors for experiments 1-20, 24-29 are used, excluding copolymerizations without solvent or in anisole. The results are presented in Table 2. Data obtained with Eq. (18) are in good agreement with Karad and Schneider's data. The system belongs to the case  $k_{22} = 0$  and  $k_{2C2} = 0$ . The only important deviation is given by the  $\alpha_{21}$  value which indicates a preference of the  $M_2$ -ended macroradical of almost one and a half times higher for CTC addition than for cross-addition.  $\alpha_{21}$  from Eq. (18) is identical with  $r_3$  from Eq. (14).  $r_3$  has been found to be zero by Karad and Schneider.

TABLE 1. Imaginary System

Equation	Reactivity ratios			
	$r_{1C}$	$r_{1C1}$	$r_{1C2}$	$r_{12}$
15	0.088	4.19	0.09	0.5
18	0.083	0.50	0.10	0.5

TABLE 2. Styrene-Difumaronitrile System

Calculation method	Reactivity ratios					
	$\alpha_{11}$	$\alpha_{12}$	$\alpha_{21}$	$\alpha_{22}$	$r_{12}$	$r_{21}$
Linear calculation [8]	3.85	0.21	0	0	0.15	0
Nonlinear calculation [8]	3.20	0.70	0	0	0.16	0
Reference 15 cited by Ref. 8	3.82	3.82	0	0	0.13	0
Eq. (18)	5.30	0.10	1.4	0	0.20	0

## DISCUSSION

Pittman and Rounsefell [9] analyze in their paper the composition-conversion data which permits the precise determination of reactivity ratio values. They conclude that such data do not exist in the literature. However, by analyzing the data in their Tables I and II [9], one can observe that conversions between 5 and 25% for optimum initial mixtures rarely generate differences in copolymer composition which can be detected by the usual analytical techniques. Also, they consider the K-value to vary with conversion. Yet, having in mind that the charge transfer copolymerization model is only a mathematical approach which neglects many phenomena such as chain transfer to solvent, even to CTC, and penultimate effects of intramolecular CTC from the growing chain, one can consider the reactivity ratios obtained by working at relatively low conversions (5-8%) and with K-values determined by a spectroscopic method to be sufficient. The validity of the model can be tested only with more detailed microstructural information: sequence distribution and configuration. For the copolymers studied by us, microstructural investigations are in progress.

The fact also to be considered is that, if  $k_{22} = 0$  (which can be seen on the Kelen-Tüdös plot), it is not necessary that  $k_{2C2}$  should be 0.

Some systems studied by us generate  $\alpha_{22} \neq 0$  [12] by the ESTIM and VERIF programs. Also, the correctness will be verified by micro-structural determinations.

The definition of  $\alpha_{ij}$  reactivity ratios is analogous to that given by Georgiev and Zubov [16] for radical alternating copolymerization, and the reactivity ratios have approximately the same physical significance: they determine the preferred mechanism by either CTC or by cross-addition.

### CONCLUSIONS

By changing the definition of reactivity ratios, a more complicated copolymerization equation is obtained. It cannot be simplified by linearization, even in most specific cases. However, especially for systems characterized by less probable homopropagation reactions, this equation suits the process better. The parameter determination can be done by the programs proposed, using Marquardt's algorithm for least-square error estimation of nonlinear parameters.

Listings of ESTIM and VERIF programs are available on request.

### REFERENCES

- [1] C. I. Simionescu, V. Percec, and A. Natansohn, Polymer, **21**, 417 (1980).
- [2] J. Seiner and M. Litt, Macromolecules, **4**, 308, 312, 314, 316 (1971).
- [3] T. Kelen and F. Tüdös, J. Macromol. Sci.-Chem., **A9**, 1 (1975).
- [4] H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., **71**, 2703 (1949).
- [5] M. W. Hanna and A. L. Ashbaugh, J. Phys. Chem., **68**, 811 (1964).
- [6] R. Foster and C. A. Fyfe, Trans. Faraday Soc., **61**, 1626 (1965).
- [7] E. Tsuchida, T. Tomono, and H. Sano, Makromol. Chem., **151**, 245 (1972).
- [8] P. Karad and C. Schneider, J. Polym. Sci., Polym. Chem. Ed., **16**, 1137 (1978).
- [9] C. U. Pittman, Jr., and T. D. Rounsefell, Macromolecules, **8**, 46 (1975).
- [10] Y. Kadoma, T. Toida, K. Takeda, K. Uno, and Y. Iwakura, J. Polym. Sci., Polym. Chem. Ed., **13**, 707 (1975).
- [11] V. Percec, A. Natansohn, and C. I. Simionescu, 29th IUPAC International Symposium on Macromolecules, Mainz, 1979, Preprints, Vol. 1, p. 345.
- [12] C. I. Simionescu, V. Percec, and A. Natansohn, J. Macromol. Sci.-Chem., **A15**, 405 (1981).

- [ 13 ] C. I. Simionescu, V. Percec, and A. Natansohn, Polym. Bull., 2, 57 (1980).
- [ 14 ] D. W. Marquardt, J. Soc. Ind. Appl. Math., 11, 431 (1963).
- [ 15 ] M. Litt and J. Radovic-Wellinghoff, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem., 17, 596 (1976).
- [ 16 ] G. S. Georgiev and V. P. Zubov, Eur. Polym. J., 14, 93 (1978).

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