ISSN 0965-545X, Polymer Science, Ser. A, 2008, Vol. 50, No. 1, pp. 74–83. © Pleiades Publishing, Ltd., 2008. Original Russian Text © T.F. Irzhak, V.I. Irzhak, G.V. Malkov, Ya.I. Estrin, E.R. Badamshina, 2008, published in Vysokomolekulyarnye Soedineniya, Ser. A, 2008, Vol. 50, No. 1, pp. 91–102.

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# Calculation of the Critical Conversion and Topological Parameters for Hyperbranched Polyisocyanurate Polymers Prepared via Cocyclotrimerization of Mono- and Diisocyanates

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**Abstract**—A new approach to the design of hyperbranched polymers, the cocyclotrimerization of mono- and diisocyanates is proposed. The kinetic scheme for the synthesis of hyperbranched polyisocyanurates was considered and calculated in the generating-function formalism. New theoretical relationships were obtained that make it possible to predict the critical conversion and a change in the structural and molecular-mass characteristics of hyperbranched polyisocyanurates in the course of the reaction, depending on the initial ratio of monoand diisocyanates and on the relative reactivity of isocyanate groups.

DOI: 10.1134/S0965545X08010124

Hyperbranched polymers represent a class of uncrosslinked three-dimensional polymers that has been intensively studied in the last decades. These polymers possess a number of unique properties distinguishing them from linear analogs, in particular, a low viscosity in solutions and melts and good solubility. In addition, hyperbranched polymers contain a large amount of functional end groups in their structure, thus allowing for further modification of the polymers to impart properties required for the manufacture of materials based on them [1].

One of the most frequently employed procedures for the synthesis of hyperbranched polymers is addition polymerization or polycondensation of type  $AB_n$ monomers  $(n \ge 2)$  containing groups A and B capable of reacting only with each other. Another, less widespread procedure for the synthesis of hyperbranched polymers is the copolymerization of bi- and polyfunctional compounds with the cessation of the reaction near the gel point. Some reports on the synthesis of hyperbranched polymers via cyclotrimerization and co-cyclotrimerization of alkynes have recently appeared in the literature [2-4]. However, among numerous studies concerning the synthesis of various hyperbranched polymers and dendrimers summarized in a number of comprehensive reviews [5-10], there are no data on the synthesis of hyperbranched polymers via the cyclotrimerization of isocyanates.

We propose a new approach to the design of hyperbranched polymers, namely, the cocyclotrimerization of di- and monoisocyanates. The process of cyclotrimerization of diisocyanates is specific in that the monomer is inherently bifunctional, but each chain propagation event in which three isocyanate groups belonging to different molecules simultaneously take part leads to an increase in functionality of the product by unity: from the initially bifunctional monomer to the trifunctional isocyanurate cyclic trimer, the tetrafunctional bicyclic pentamer, etc. (Fig. 1).

Since all end groups are capable of reacting with one another (unlike the  $AB_n$  system), gelation, in principle, should begin already at a 50% conversion of the diisocyanate isocyanate groups. The pregel product can be considered a hyperbranched polymer, with the relative amount of the reactant diisocyanate and *n*-mers in the reaction mixture being close to the statistical value at this step. The reaction mixture obtained in this manner, either as such or after blocking the terminal isocyanate groups, is a precursor for the preparation of the crosslinked polymers polyisocyanurates (PICs). These polymers possess high heat and fire resistance, stability against corrosive environments and organic solvents, atmospheric and radiation resistance, high adhesion to various substrates, and good insulating properties.

Our approach to the synthesis of new hyperbranched PICs via the cocyclotrimerization of mono- and diisocyanates suggests a decrease in the initial functionality *f*. Depending on the concentration ratio of the monomers, the functionality can vary from 1 to 2. This variation should result in a delayed growth of the functionality of the reaction mixture; a displacement of the gel point toward higher conversions of isocyanate groups up to 100% (Fig. 1, at  $n_1 > 2n_2$ ); and, hence, an



**Fig. 1.** Scheme of formation of hyperbranched polyisocyanurates. R and R' are alkyl, aryl, or alkylaryl; Y is a functional group that does not react with the isocyanate group;  $n_1$  is the mole fraction of monoisocyanate; and  $n_2$  is the mole fraction of diisocyanate: (1) cyclotrimerization of diisocyanate and (2) cocyclotrimerization of mono- and diisocyanates.

increase in the molecular mass of the hyperbranched polyisocyanurate that is formed before the gel point. The presence of monoisocyanate under these conditions facilitates the formation of linear or terminal fragments of the polymer molecule.

The results of studies on the cyclotrimerization and cocyclotrimerization reactions of various diisocyanates are summarized in a number of reviews [11-13]. It should be noted that most of the reports concern the selection of catalysts and investigation of their effect on the diisocyanate cyclotrimerization kinetics. Assumptions about the mechanism of the reaction have been made in these reports. The studies of cocyclotrimerization of mono- and diisocyanates [14–20] focused on the kinetic behavior of the reaction and determination of the cocyclotrimer composition, although the molecular-mass characteristics and certain mechanical properties of PICs were determined in some cases. However, nobody has attempted to study the structure and properties of polymers that are formed before the gel point during the cocyclotrimerization of mono- and diisocyanates, and the process itself was not considered a procedure for the synthesis of hyperbranched polymers. Systems of this kind, which are nontrivial in both theoretical and experimental aspects, have not been analyzed yet. The objective of this study was to calculate the gelling point and certain topologically significant structural and molecular-mass parameters of hyperbranched polyisocyanurates produced in the cyclotrimerization and cocyclotrimerization of isocyanates.

#### STARTING MODEL

The isocyanate groups of monomers involved in the cocyclotrimerization reaction may be close, as in the 1,6-hexamethylene diisocyanate-1-chloro hexamethylene 6-isocyanate (CHMI) pair [14–16], or differ, as in the pair aromatic tolylene 2,4-diisocyanate-aliphatic CHMI, in reactivity. Thus, the scheme of the cocyclotrimerization reaction of mono- and diisocyanates with different reactivities of all NCO groups can include 10 rate constants even without allowance for the effect of substituents; if a change in reactivity of the second isocyanate group of diisocyanate after the conversion of the first group (the so-called first shell substitution effect, this effect is especially strong for aromatic diisocyanates [21]) is taken into account, the number of rate constants increases to 35 (Fig. 2). Of course, it is practically impossible to solve the system of rate equations in the latter case; therefore, we assume that the reactivity of isocyanate groups remains unchanged.

In the simplest version, the general scheme of the cocyclotrimerization of mono- and diisocyanates having NCO groups that differ in reactivity without allowance for the substituent effect is as given below.



**Fig. 2.** Kinetic scheme for the formation of polyisocyanurates: (a) cocyclotrimerization of mono- and diisocyanates having different reactivities of NCO groups of types A, B, and C and (b) cocyclotrimerization of mono- and diisocyanates with participation of oligomers at different reactivities of NCO groups of types A, B, C, A', and B'. The type and reactivity of the isocyanate group in the oligomer changed (from A to A' and from B to B') after the entry of one of the diisocyanate groups into the cocyclotrimerization reaction (B or A, respectively).

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Cyclotrimerization of three molecules of monofunctional monomers:

$$R(1, c) + R(1, c) + R(1, c) \xrightarrow{k} R(3, 0),$$
$$(k = k_{ccc}).$$

Cocyclotrimerization of two molecules of a monofunctional monomer and one molecule of an  $m_i$ -functional monomer and/or oligomer:

$$R(1, c) + R(1, c) + R(n, a, b) \xrightarrow{k} R(n', a', b'),$$

where n' = n + 2, a' = a - 1, b' = b, and  $k = k_{acc}$  or a' = a, b' = b - 1, and  $k = k_{bcc}$ .

Cocyclotrimerization of one molecule of a monofunctional monomer and two molecules of  $m_i$ -functional monomers and/or oligomers:

$$\mathbf{R}(1, c) + \mathbf{R}(n_1, a_1, b_1) + \mathbf{R}(n_2, a_2, b_2) \stackrel{k}{\longrightarrow} \mathbf{R}(n', a', b').$$

Here,  $n' = n_1 + n_2 + 1$ ,  $a' = a_1 + a_2 - 2$ ,  $b' = b_1 + b_2$ , and  $k = k_{aac}$ ;  $a' = a_1 + a_2 - 1$ ,  $b' = b_1 + b_2 - 1$ , and  $k = k_{abc}$ ; or  $a' = a_1 + a_2$ ,  $b' = b_1 + b_2 - 2$ , and  $k = k_{bbc}$ .

Cocyclotrimerization of three molecules of  $m_i$ -functional monomers and/or oligomers:

$$R(n_1, a_1, b_1) + R(n_2, a_2, b_2)$$
  
+  $R(n_3, a_3, b_3) \xrightarrow{k} R(n', a', b')$ 

where  $n' = n_1 + n_2 + n_3$ ,  $a' = \Sigma a - 3$ ,  $b' = \Sigma b$ , and  $k = k_{aaa}$ ;  $a' = \Sigma a - 2, b' = \Sigma b - 1, \text{ and } k = k_{aab}; a' = \Sigma a - 1,$  $b' = \Sigma b - 2$ , and  $k = k_{abb}$ ; or  $a' = \Sigma a$ ,  $b' = \Sigma b - 3$ , and  $k = k_{bbb}$ .

Hereinafter, R(n, a, b) is the  $m_i$ -functional monomer or oligomer and its concentration; n is the number of units in a macromolecule, wherein  $n = 1, 3, 5, ...; m_i$  is the functionality of the oligomer, where  $m_i = a_i + b_i$ ; a is the number of isocyanate groups of type A (having a reactivity conventionally taken as a), a = 0, 1, 2, ...; bis the number of isocyanate groups of type B (having a reactivity conventionally taken as b), b = 0, 1, 2, ...;R(1, c) is the reactant monofunctional isocyanate and its concentration, wherein c characterizes the type of functional groups, rather than their number, since R(1, c) always contains only one isocyanate group C (i.e., c = 1); and  $k_{aaa}$ ,  $k_{aab}$ ,  $k_{abb}$ , etc., are the corresponding rate constants, which are determined by the reactivity of reacting NCO groups, where the three-character subscript denotes the types of the groups involved in the reaction:  $k_{ccc}$  for C + Č + C,  $k_{bbc}$  for C + B + B,  $k_{abc}$  for A + B + C. etc.

It is obvious that this scheme does not reflect the kinetics of the process in the strict sense (conversion with time); rather, it characterizes the structural kinetics (structure parameters as a function of conversion).

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To take account of the differences in the reactivity of NCO groups, it should be borne in mind that, although the catalytic cyclotrimerization of isocyanates follows the first-order rate law, the reaction can be represented as trimolecular over a certain fictitious time. It is known that, independently of the chemical specifics of its mechanism, any reaction can be represented as nmolecular within the frame of a certain fictitious time [22], where *n* is the number of reactants that take part in the reaction. The question of whether a complex reaction mechanism can hamper the formulation of rate equations seems to have been first raised by Stanford and Stepto [23]. To resolve the problem, the cited authors proposed to use as an independent variable conversion instead of time. Thus, it is the conversion that is in fact the fictitious time.

With allowance for the additivity of the free energy of activation, i.e., on the assumption that the rate constant  $k_{abc}$  of the reaction A + B + C can be expressed as

$$k_{abc} = k_a k_b k_c,$$

 $\mathbf{\Gamma}$ 

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we have

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$$F = k_a A + k_b B + k_c C,$$

$$\frac{dR(1,1)}{dt} = -k_c R(1,1)F^2,$$

$$\frac{dR(1,1,1)}{dt} = -(k_a + k_b)R(1,1,1)F^2,$$

$$\frac{dR(3,0,0)}{dt} = \frac{1}{3}k_c^3R(1,1)^3,$$

$$\frac{dR(3,1,0)}{dt}$$

$$= k_b R(1,1,1)k_c^2R(1,1)^2 - k_a R(3,1,0)F^2,$$

$$\frac{dR(3,0,1)}{dt}$$

$$= k_a R(1,1,1)k_c^2R(1,1)^2 - k_b R(3,0,1)F^2,$$

$$\frac{dR(3,2,0)}{dt}$$

$$= k_b^2 R(1,1,1)^2 k_c R(1,1) - 2k_a R(3,2,0)F^2,$$

$$\frac{dR(3,0,2)}{dt}$$

$$= k_a^2 \mathbf{R}(1, 1, 1)^2 k_c \mathbf{R}(1, 1) - 2k_b \mathbf{R}(3, 0, 2) F^2,$$

$$\frac{dR(3, 1, 1)}{dt} = (k_a + k_b)R(1, 1, 1)^2 k_c R(1, 1) -(k_a + k_b)R(3, 1, 1)F^2,$$
  
$$\frac{dR(3, 3, 0)}{dt} = \frac{1}{3}k_b^3R(1, 1, 1)^3 - 3k_aR(3, 3, 0)F^2, \frac{dR(3, 2, 1)}{dt} = \frac{1}{3}(k_a + k_b^2)R(1, 1, 1)^3 - (2k_a + k_b)R(3, 2, 1)F^2, \frac{dR(3, 1, 2)}{dt} = \frac{1}{3}(k_a^2 + k_b)R(1, 1, 1)^3 - (k_a + 2k_b)R(3, 1, 2)F^2, \frac{dR(3, 0, 3)}{dt} = \frac{1}{3}k_a^3R(1, 1, 1)^3 - 3k_bR(3, 0, 3)F^2,$$

etc.

In general, for  $n \ge 3$  in R(n, a, b), the rate equation takes the form

$$\frac{dR(n, a, b)}{dt} = -(ak_a + bk_b)R(n, a, b)F^2$$

$$+k_c^2R(1, c)^2(k_a(a+1)R(n-2, a+1, b))$$

$$+k_b(b+1)R(n-2, a, b+1))$$

$$+\frac{1}{2}k_cR(1, c)\left\{k_a^2(a+2)^2\sum_{i=1}^{n-2}R(i, a+2, b)\right\}$$

$$\times R(n-i-1, a+2, b)\right\}$$

$$+\frac{1}{2}k_cR(1, c)\left\{k_ak_b(a+1)(b+1)\right\}$$

$$\times \sum_{i=1}^{n-2}R(i, a+1, b+1)R(n-i-1, a+1, b+1)\right\}$$

$$+\frac{1}{2}k_cR(1, c)\left\{k_b^2(b+2)^2\right\}$$

$$\times \sum_{i=1}^{n-2} \mathbb{R}(i, a, b+2) \mathbb{R}(n-i-1, a, b+2) \bigg\}$$
(1)  
+  $\frac{1}{3} \sum_{i=1}^{n-2n-i-1} \sum_{j=1}^{n-2n-i-1} k_a^3 (a+3)^3 \mathbb{R}(i, a+3, b)$   
×  $\mathbb{R}(j, a+3, b) \mathbb{R}(n-i-j, a+3, b)$   
+  $\frac{1}{3} \sum_{i=1}^{n-2n-i-1} \sum_{j=1}^{n-2n-i-1} k_a^2 k_b (a+2)^2 (b+1) \mathbb{R}(i, a+2, b+1)$   
×  $\mathbb{R}(j, a+2, b+1) \mathbb{R}(n-i-j, a+2, b+1)$   
+  $\frac{1}{3} \sum_{i=1}^{n-2n-i-1} \sum_{j=1}^{n-2n-i-1} k_a k_b^2 (a+1) (b+2)^2 \mathbb{R}(i, a+1, b+2)$   
×  $\mathbb{R}(j, a+1, b+2) \mathbb{R}(n-i-j, a+1, b+2)$   
+  $\frac{1}{3} \sum_{i=1}^{n-2n-i-1} \sum_{j=1}^{n-2n-i-1} k_b^3 (b+3)^3 \mathbb{R}(i, a, b+3)$   
×  $\mathbb{R}(j, a, b+3) \mathbb{R}(n-i-j, a, b+3)$ .

## CALCULATION PROCEDURE

Systems with a large number of differential equations can be solved only in the convoluted form. The simplest way of solution is the use of generating functions

$$\Phi(s,q,r) = \sum_{n,a,b} s^n q^a r^b \mathbf{R}(n,a,b),$$

where s, q, and r are independent variables.

The application of this method makes it possible to transform Eq. (1) into the set of equations

$$\frac{d\mathbf{R}(1,c)}{dt} = -k_c \mathbf{R}(1,c) [k_c \mathbf{R}(1,c) + k_a \mathbf{A} + k_b \mathbf{B}]^2,$$

$$\frac{\partial \Phi(s,q,r)}{\partial t} = -\left[k_a q \frac{\partial \Phi}{\partial q} + k_b r \frac{\partial \Phi}{\partial r}\right] \qquad (2)$$

$$\times \left[k_c \mathbf{R}(1,c) + k_a \mathbf{A} + k_b \mathbf{B}\right]^2$$

$$+ \frac{1}{3} \left[k_c s \mathbf{R}(1,c) + k_a \frac{\partial \Phi}{\partial q} + k_b \frac{\partial \Phi}{\partial r}\right]^3$$

with the initial conditions  $R(1, c) = C_0$ ,  $\Phi(1, 1, 1) = sqrA_0$ ,  $A_0 = B_0$ , and  $A_0 + C_0 = N_0$ , where  $A_0$ ,  $B_0$ , and  $C_0$  are the initial concentrations (in g-equiv/l) of NCO groups of types A, B, and C, respectively;  $N_0$  is the initial total concentration of mono- and diisocyanates

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(mol/l); and  $k_a$ ,  $k_b$ , and  $k_c$  are the components of the corresponding kinetic constants.

From set (2), we transfer to set of equations (3) for the moments of the generating function:

$$R(1, c) = C,$$
  

$$\Phi(1, 1, 1) = N - C,$$
  

$$\frac{\partial \Phi(1, 1, 1)}{\partial s} \equiv \Phi_s = M - C,$$
  

$$\frac{\partial \Phi(1, 1, 1)}{\partial q} \equiv \Phi_q = A,$$
  

$$\frac{\partial \Phi(1, 1, 1)}{\partial r} \equiv \Phi_r = B.$$

Here, *M* denotes the total concentration of polymer and monomers (mol/l), which is equal to  $N_0$ ; M - C is the polymer concentration (mol/l); *A*, *B*, and *C* are the concentrations of NCO groups of types A, B, and C (g-equiv/l), respectively; and *N* is the total concentration of mono- and diisocyanates (mol/l).

With the use of this system, it is possible to calculate the number-average degree of polymerization  $P_n$  and functionality  $f_n$ :

$$P_{n} = \Phi_{s} / \Phi(1, 1, 1) = (M - C) / (N - C),$$
  
$$f_{n} = (\Phi_{q} + \Phi_{r}) / \Phi(1, 1, 1) = (A + B) / (N - C).$$

The second moments of the generating function

$$\frac{\partial^2 \Phi(1,1,1)}{\partial i \partial j} \equiv \Phi_{ij}$$

(i, j = s, q, r) make it possible to find the weight-average degree of polymerization  $P_w$  and functionality  $f_w$ :

$$P_{w} = \frac{\Phi_{ss}}{\Phi_{s}} + 1,$$

$$f_{w} = \frac{\Phi_{qq} + 2\Phi_{qr} + \Phi_{rr}}{\Phi_{q} + \Phi_{r}} + 1,$$

$$\frac{dC}{dt} = -k_{c}C(k_{a}A + k_{b}B + k_{c}C)^{2},$$

$$1, 1, 1) = -(k_{c}A + k_{c}B)(k_{c}A + k_{c}B + k_{c}C)^{2},$$

$$\frac{d\Phi(1,1,1)}{dt} = -(k_a A + k_b B)(k_a A + k_b B + k_c C)^2 + \frac{1}{3}(k_a A + k_b B + k_c C)^3,$$

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$$\begin{aligned} \frac{d\Phi_s}{dt} &= k_c C (k_a A + k_b B + k_c C)^2, \\ \frac{d\Phi_q}{dt} &= -k_a A (k_a A + k_b B + k_c C)^2, \\ \frac{d\Phi_r}{dt} &= -k_b B (k_a A + k_b B + k_c C)^2, \\ \frac{d\Phi_{ss}}{dt} &= 2 [k_c C + k_a \Phi_{sq} + k_b \Phi_{sr}]^2 \\ \times [k_c C + k_a A + k_b B], \\ \frac{d\Phi_{sq}}{dt} &= -k_a \Phi_{sq} [k_c C + k_a A + k_b B]^2 \\ + 2 [k_c C + k_a \Phi_{sq} + k_b \Phi_{sr}] [k_c C + k_a A + k_b B] \\ \times (k_a \Phi_{qq} + k_b \Phi_{qr}), \\ \frac{d\Phi_{sr}}{dt} &= -k_b \Phi_{sr} [k_c C + k_a A + k_b B]^2 \\ + 2 [k_c C + k_a \Phi_{sq} + k_b \Phi_{sr}] [k_c C + k_a A + k_b B]^2 \end{aligned}$$
(3)

 $+2[k_a\Phi_{aa}+k_b\Phi_{ar}](k_a\Phi_{ar}+k_b\Phi_{rr})[k_cC+k_aA+k_bB],$ 

 $\times (k_a \Phi_{ar} + k_b \Phi_{rr}),$ 

 $\frac{d\Phi_{qq}}{dt} = -2k_a\Phi_{qq}[k_cC + k_aA + k_bB]^2$ 

 $+ 2[k_a \Phi_{qq} + k_b \Phi_{qr}]^2 [k_c C + k_a A + k_b B],$ 

 $\frac{d\Phi_{qr}}{dt} = -(k_a + k_b)\Phi_{qr}[k_cC + k_aA + k_bB]^2$ 

$$\frac{d\Phi_{rr}}{dt} = -2k_b\Phi_{rr}[k_cC + k_aA + k_bB]^2$$
$$+ 2[k_a\Phi_{qr} + k_b\Phi_{rr}]^2[k_cC + k_aA + k_bB]$$

at the initial conditions

$$\Phi_s = \Phi_q = \Phi_r = A_0 = B_0,$$
  
$$\Phi_{ss} = 0, \quad \Phi_{sq} = A_0, \quad \Phi_{sr} = B_0,$$
  
$$\Phi_{qq} = 0, \quad \Phi_{qr} = A_0, \quad \Phi_{rr} = 0.$$

t = 0,

In the absence of the substituent effect, the probabilistic approach to the calculation of characteristics of the topological structure of the products can be used. The main characteristic of this sort for hyperbranched polymers is the degree of branching  $D_B$ , which actually defines the proportion of dendritic units in the total amount of polymer units and is expressed as follows [24]:

$$D_B = \frac{B+T}{L+B+T},$$

where *B*, *T*, and *L* are the relative amounts of branched, terminal, and linear fragments in the polymer chain, respectively.

Then, in the case of equal reactivity of isocyanate groups, the degree of branching is defined by

$$D_B = \frac{(1-n_1)^2 \alpha^2 + 3[(1-n_1)(1-\alpha) + n_1]^2}{(1-n_1)^2 \alpha^2 + 3[(1-n_1)(1-\alpha) + n_1]^2 + 3(1-n_1)\alpha[(1-n_1)(1-\alpha) + n_1]}$$

Here,  $n_1$  is the mole fraction of monoisocyanate in the mixture,  $\alpha$  is the conversion of isocyanate groups,  $(1 - n_1)^3 \alpha^3$  is the probability for the formation of the branched fragment (junction),  $3(1 - n_1)\alpha[(1 - n_1)(1 - \alpha) + n_1]^2$  is the probability for the formation of the terminal fragment (tail), and  $3(1 - n_1)^2\alpha^2[(1 - n_1)(1 - \alpha) + n_1]$  is the probability for the formation of the linear fragment.

## PREDICTION OF SYNTHESIS RESULTS

By means of numerical integration of set (3) of differential equations in terms of the above calculation formalism, we attempted to predict the molecular-mass characteristics, the degree of branching of hyperbranched polyisocyanurates, and the critical conversion of isocyanate groups (gel point). Used as initial data in this calculation were easily controllable or preliminar-



**Fig. 3.** Dependence of  $P_n$  on  $\alpha$  during cocyclotrimerization at the same reactivity of all isocyanate groups  $(k_a = k_b = k_c)$  and monoisocyanate mole fractions of  $n_1 = (1)$  0, (2) 0.333, (3) 0.57, (4) 0.666, (5) 0.75, (6) 0.889, and (7). 1.0.

ily known parameters: the initial concentrations of diand monoisocyanates, the reactivity ratio of isocyanate groups, and the conversion of isocyanate groups  $\alpha$  to which the cyclotrimerization reaction is conducted.

The gel point (critical conversion of isocyanate groups  $\alpha_{cr}$ ) was determined as described in [25] as a point of steep rise in the second moments of the generating function.

The topological parameters of hyperbranched PICs were calculated by limiting the machine time to a value close to the critical one.

The dependence of the number-average degree of polymerization  $P_n$  on the conversion  $\alpha$  for the case of equal reactivity of all isocyanate groups ( $k_a = k_b = k_c$ ) can be expressed as follows

$$P_{\rm n} \propto (1-\alpha)^{-1}$$
.

This relationship makes it possible to judge the magnitude of the critical conversion of isocyanate groups  $\alpha_{cr}$ ; the curves terminate at the gel point (Fig. 3). From Fig. 3, it is seen that, as the monoisocyanate concentration in the initial mixture increases, the maximum attainable yield of hyperbranched polymers increases to 100% (at a monoisocyanate mole fraction of  $n_1 \ge 0.66$ ) with a simultaneous steep rise in the number-average degree of polymerization.

According to the data presented in Fig. 4, near the threshold concentration of the monofunctional reactant  $(n_1 \approx 0.66)$  at an extent of conversion of  $\alpha \approx 1$ , the degree of polymerization has a maximum value, the degree of branching  $D_B$  is greater than 0.5, and the number-average functionality  $f_n$  tends to zero. In Fig. 4, the conversion of isocyanate groups is close to the critical value before the break of the curves and is  $\alpha \approx 1$  after the break.

From Fig. 5, which presents the structural characteristics  $P_w$  and  $f_w$  of the branched products at  $\alpha \longrightarrow \alpha_{cr}$ , with allowance for equal reactivity of all isocyanate groups involved in the reaction, it follows that the scaling relation

$$P_{\rm w}, f_{\rm w} \propto \left(\alpha - \alpha_{\rm cr}\right)^{-1}$$
.



**Fig. 4.** Dependence of (1)  $P_n$ , (2)  $f_n$ , and (3)  $D_B$  on the monoisocyanate mole fraction  $n_1$  at  $\alpha = \alpha_{cr}$  and identical reactivities of all isocyanate groups.

holds near the gel point.

Consequently, it may be assumed with a high confidence that the products resemble critical clusters in the character of distribution. Note that this is the result of kinetic calculation, not percolation analysis.

In addition, it should be noted that this result is fully consistent with the conclusions of the Flory–Stockmayer statistical theory [23, 26], although certain experimental data [27–29] suggest that the power index may be substantially higher in absolute value, from -1.5 to -2.7. The percolation theory [30] gives this quantity as -1.76. Obviously, the matter is that neither the statistical theory nor our kinetic calculation takes into account the possibility of ineffective cyclization during gelation.

From Fig. 6, it is seen that the products have broad molecular-mass and functionality distributions. The polydispersity index steeply increases with an approach to the gel point. Note that such a dependence of  $P_w/P_n$ on  $\alpha$  does not hold for curves 4 and 5 (at a monoisocyanate mole fraction of  $n_1 \ge 0.7$ ), since there is no gelling at a conversion close to unity. At the same time, the pattern of the dependence of the functionality distribution on conversion remains unchanged for curves 4' and 5'. This invariability is due to the fact that, despite the decrease in  $f_w$ ,  $f_n$  tends to zero at a higher rate.

A comparison of the data presented in Figs. 3–6 shows that there is a sophisticated dependence of  $f_w$ ,  $f_n$ ,  $P_w$ , and  $P_n$  on the amount of monoisocyanate in the initial reaction mixture.

The value of the critical conversion is strongly affected by not only the concentration of monoisocyan-



**Fig. 5.** Dependence of  $(1-3) P_w$  and  $(1'-3') f_w$  on conversion  $\alpha$  at  $\alpha$  tending to  $\alpha_{cr}$ ; identical reactivities of all NCO groups; and  $n_1 = (1, 1') 0.18, (2, 2') 0.57$ , and (3, 3') 0.66.

ate but also its reactivity. As an example, Fig. 7 presents the dependence of the critical conversion of isocyanate groups  $\alpha_{cr}$  on the mole fraction of monoisocyanate in the initial reactant mixture  $n_1$  with varying reactivity of the monoisocyanate NCO group  $k_c$  on the assumption that both NCO groups in the diisocyanate have equal reactivity ( $k_a = k_b$ ). Note the unusual character of the  $\alpha_{cr}-n_1$  curve: the critical conversion decreases with an increase in the concentration of a chain terminating agent, the monofunctional reactant, in the case of its low reactivity  $k_c < 1$ . This behavior is due to the fact that the gel is formed mainly by the bifunctional agent; thus,  $\alpha_{cr}$  lowers because of a decrease in its relative amount in the mixture.

The results of calculation of the critical conversion of isocyanate groups  $\alpha_{cr}$  as a function of the monoisocyanate mole fraction in the initial mixture  $n_1$  with varying reactivity of one of the diisocyanate NCO groups  $k_b$  (Fig. 8) indicate that a decrease or increase in  $k_b$  leads to a growth in  $\alpha_{cr}$  at constant  $n_1$  but has a slight effect on the threshold value of  $n_1$  at which  $\alpha_{cr} = 1$ . In the calculation, the reactivity of the second NCO group in the diisocyanate was taken equal to the reactivity of the monoisocyanate NCO groups ( $k_a = k_c$ ).

Thus, the results indicate that, in order to attain the maximum value of  $P_n$  in the synthesis of hyperbranched polymers via the cocyclotrimerization of mono- and diisocyanates, it is necessary to carry out the reaction as close as possible to the critical conversion at the lowest practicable concentrations of the monoisocyanate. The concentration of the monoisocyanate as a chain terminating agent should be selected in such a manner that,



**Fig. 6.** Dependence of (1-5) the polydispersity index  $P_w/P_n$  and (1'-5') functionality distribution  $f_w/f_n$  on conversion  $\alpha$  at identical reactivities of all NCO groups and  $n_1 = (1, 1') 0, (2, 2') 0.4, (3, 3') 0.6, (4, 4') 0.8$ , and (5, 5') 1.

on the one hand, the polymer products will be obtained with the highest yield (an increase in the monoisocyanate concentration, and hence, in  $\alpha_{cr}$ ) and, on the other hand,  $M_w$  of the macromolecules will have the maximum value (an increase in diisocyanate concentration).





**Fig. 7.** Dependence of  $\alpha_{cr}$  on  $n_1$  and the reactivity of monoisocyanate ( $0.1 \le k_c \le 10$ ) at equal reactivities of both isocyanate groups of diisocyanate ( $k_a = k_b = 1$ ).



**Fig. 8.** Dependence of  $\alpha_{cr}$  on  $n_1$  and the reactivity of one of the diisocyanate functional groups  $(0.1 \le k_b \le 10)$  at equal reactivities of the second diisocyanate NCO group and the monoisocyanate NCO group  $(k_a = k_c = 1)$ .

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effect on both the yield and topology of the product polymers.

CONCLUSIONS

On the basis of the results of the calculations, it may be assumed that the optimal mole fraction of monoisocyanate for the preparation of hyperbranched polyisocyanurates via the cocyclotrimerization reaction of mono- and diisocyanates having equal reactivities of all isocyanate groups with a conversion of 100% and the maximal molecular mass is  $n_1 \approx 0.66$ . However, in the case of different reactivities of NCO groups of monoand diisocyanates, the optimal conditions may vary, and the data obtained in this study will be useful for designing such experiments. These data will also be necessary for the assessment of the contribution of side reactions and other factors that have been ignored in this investigation but may affect the structure and the molecular-mass distribution of hyperbranched PICs. In addition, the established relationships can be used for the prediction of the critical conversion and properties of the cyclotrimerization and cocyclotrimerization products of not only isocyanates but also alkynes, which are currently used in the synthesis of hyperbranched polymers.

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