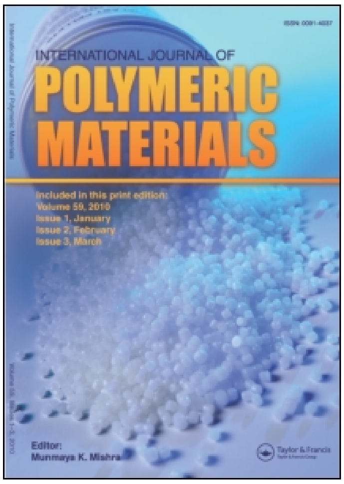


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

The Formation of the Polyisocyanurate Networks Structure

E. R. Badamshina[a]; V. A. Grigorieva[a]; V. V. Komratova[a]; A. I. Kuzaev[a]; Yu. A. Ol'khov[a]; V. P. Lodygina[a]; G. A. Gorbushina[a]; S. M. Baturin[a]
[a] Russian Academy of Science, Institute of Chemical Physics in Chernogolovka,

To cite this Article Badamshina, E. R. , Grigorieva, V. A. , Komratova, V. V. , Kuzaev, A. I. , Ol'khov, Yu. A. , Lodygina, V. P. , Gorbushina, G. A. and Baturin, S. M.(1993) 'The Formation of the Polyisocyanurate Networks Structure', International Journal of Polymeric Materials, 19: 1, 117 — 125

To link to this Article: DOI: 10.1080/00914039308012023

URL: http://dx.doi.org/10.1080/00914039308012023

Intern. J. Polymeric Mater., 1993, Vol. 19, pp. 117–125
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

The Formation of the Polyisocyanurate Networks Structure

E. R. BADAMSHINA, V. A. GRIGORIEVA, V. V. KOMRATOVA, A. I. KUZAEV, YU. A. OL'KHOV, V. P. LODYGINA, G. A. GORBUSHINA and S. M. BATURIN

Russian Academy of Science, Institute of Chemical Physics in Chernogolovka

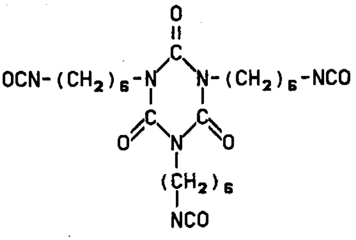
(Received July 3, 1992)

The reactions of PCT and CPCT of aliphatic isocyanates in the presence of catalysts HBSO and CN-DMSO were found to obey the first-order law. The observed rate constants at various temperatures and catalyst concentrations, the activation energy were determined. It was shown that in the PCT process with above catalysts practically only one type of a cyclic structure (isocyanurate) was formed. The HMDI PCT gives a highly cross-links polymer, the cross-links density of a network being equal to $\upsilon = 26 \times 10^{-4}$ mol/cm^3. In CPCT the polyisocyanurates with various cross-links density of a polymer network were obtained. At different ratios of mono- and diisocyanate the molecular-mass parameters of the interunit chains were determined, their effect on physico-mechanical properties of polyisocyanurates was established.

KEY WORDS Polyisocyanurate, networks, structure trimers

The ability of isocyanates to polymerize at =C=N— bond with the formation of linear polymers, cyclic dimers (uretidindions) and cyclic trimers (isocyanurates) is well-known. The polycyclotrimerization (PCT) reaction of diisocyanates and especially aliphatic ones is of interest for synthesis of polymers with regular structure and alternating isocyanurate fragments (polyisocyanurate networks).

In the present paper the process of the polyisocyanurate networks formation has been studied on the PCT reaction of 1.6-hexamethylendiisocyanate (HMDI). Isocyanurate three-functional trimers of the type (1) are formed at the initial stage of the HMDI PCT. Further they give penta-, hepta-, *n*-mers and at the degree of the NCO-groups conversion $\alpha > 0.5$—the cross-linked structure.


(1)

The PCT reactions of the isocyanates are known[1] to proceed in the presence of various catalysts. In this work hexa-*n*-butyldistannum oxide (HBSO) and cobalt

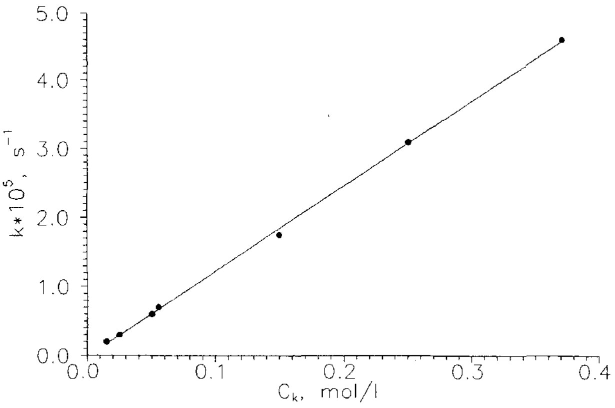


FIGURE 1 The dependence of the observed reaction rate constant on the HBSO concentration ($T = 353$ K).

naphtenate (CN)-dimethylsulfoxide (DMSO) system have been used as the catalysts (toluene solution—8% by weight of CN, with mole ratio of [DMSO]/[CN] 5.4–5.5 was used as the second catalytic system). HBSO is a rather weak catalyst for HMDI PCT as it is seen from the dependence of the observed reaction rate constant on HBSO concentration (Figure 1). The catalytic system CN-DMSO allows to decrease the temperature of the PCT reaction. Thus, the observed rate constant of HMDI PCT in the presence of 2% by weight of HBSO at 353 K is 6.1×10^{-6} s^{-1}, of 2% by weight of CN-DMSO at 343 K is 12.5×10^{-6} s^{-1}. These catalysts were chosen due to their selectivity, i.e. their ability to form mainly one type of a cyclic structure (isocyanurate structure) in the reaction. The spectral and chromatographic analyses confirm it. The spectra of oligoisocyanurates have absorption bands of the NCO-groups (2270 cm^{-1}) as well as the isocyanurate carbonyl groups (1678 cm^{-1}). Practically there is no absorption band at 1768 cm^{-1} that corresponds to carbonyl of uretidindion cycle.[2] In all chromatograms for oligoisocyanurates and sol-fractions of network polyisocyanurates there is no peak that corresponds to the HMDI dimer.

The gel permeation chromatography (GPC) method was used for the first time in our laboratory to study the PCT reaction of isocyanates. This method allows to control the kinetics of monomer consumption, to determine the reaction mixture composition during the process and molecular-mass characteristics of the reaction products. To obtain quantitative results from the chromatograms a calibration dependence V_R (lg M) has been plotted where V_R is the retention volume, M is molecular mass. The retention volumes for tri-, penta-, heptamers of HMDI were established by the repeated fractionation of the oligoisocyanurate samples treated by methanol using the GPC method. In addition we have experimentally determined V_R values for the HMDI urethane derivatives (HMDI was treated by methanol, ethanol and decanol), 1-chlorohexamethylene-6-isocyanate (CHMI) and its trimer, 2.4-toluilendiisocyanate after their interaction with methanol. The corresponding molecular masses were calculated taking into account the solvate shells.[3] While interpreting the gel-chromatograms the correction because of the change of the refraction index depending on the oligomer molecular mass was introduced.[4]

By comparison of the oligoisocyanurates gel-chromatograms with the calibration dependence the composition of reaction mixture (weight parts of monomer, trimer and polymer) was found at various stages of the HMDI PCT. These weight parts were calculated by the ratio between the area of the corresponding peak and the area of the whole chromatogram. The dependences of these weight parts on the conversion degree of the HMDI PCT in bulk in the presence of HBSO are given in Figure 2.

Table I gives molecular-mass characteristics of oligoisocyanurates (average numerical molecular mass $\bar{M}_n$ and polydispersion coefficient $\bar{M}_w/\bar{M}_n$ of the polymeric portion and the whole sample including monomer and trimer) at different stages of HMDI conversion. As it is seen from the Table the increase in α causes increase in $\bar{M}_n$ both of the polymeric portion and of the whole oligomer. The polydispersion of the whole sample equal to 2 at $\alpha \simeq 0.5$, while $\bar{M}_w/\bar{M}_n$ of the polymeric portion changes little in the range of 1.01–1.15.

It should be noted that the composition of the reaction mixture is determined by the conversion degree and does not depend on a catalyst concentration and a

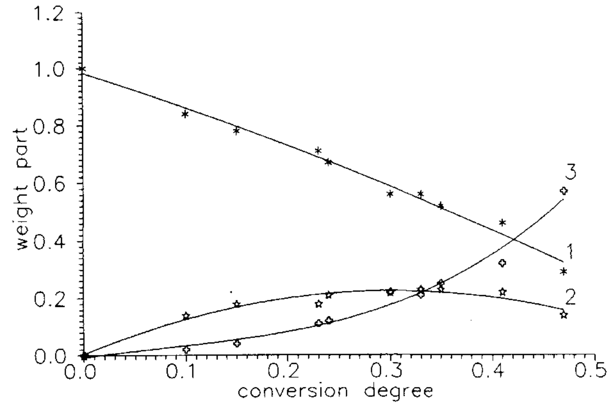


FIGURE 2 The dependence of the HMDI (1), trimer (2) and polymer (3) weight parts on the conversion degree of the HMDI PCT (catalyst-HBSO).

TABLE I

Composition and molecular-mass characteristics of oligoisocyanurates at the various conversion degrees of PCT HMDI

α	T,K	[HBSO] %	weight parts			total		polym.part	
			HMDI	trim.	polym.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.10	395	2.1	0.84	0.14	0.02	276	1.16	951	1.01
0.15	379	2.1	0.78	0.18	0.04	289	1.22	943	1.01
0.23	353	1.2	0.71	0.18	0.11	341	1.38	1040	1.02
0.30	353	2.1	0.56	0.22	0.22	402	1.58	1120	1.07
0.35	353	1.2	0.52	0.23	0.25	431	1.61	1210	1.06
0.41	379	2.1	0.46	0.22	0.32	476	1.71	1270	1.08
0.47	379	2.1	0.29	0.14	0.57	718	2.03	1690	1.15

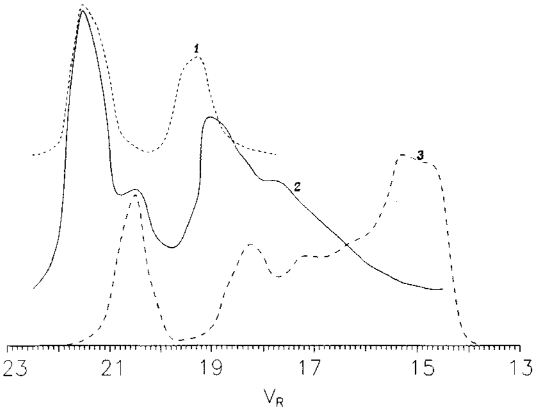


FIGURE 3 The oligoisocyanurate gel-chromatograms at the conversion degree $\alpha = 0.45$: $\rho_1 = 1$ (1), $\rho_1 = 0.5$ (2), $\rho_1 = 0$ (3).

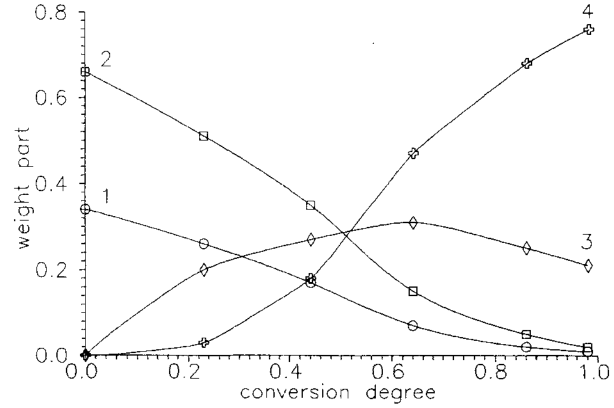


FIGURE 4 The dependence of HMDI (1), CHMI (2), trimers (3) and polymer (4) weight parts on the conversion degree of CPCT ($\rho_1 = 0.5$).

reaction temperature. The analysis of gel-chromatograms showed that monomer and trimer are present in the reaction mixture far behind the point of the gel-formation. This conclusion is quite consistent with the kinetic results which were obtained by the calorimetric method, that allows to study the kinetics of the reaction till high degrees of conversion ($\alpha > 0.9$).

The good straightening of kinetic curves in coordinates of the first order reaction equation till high degrees of conversion indicates that reactivity of isocyanate groups does not depend on what molecule it is joined to—monomer, trimer, etc. The activation parameters of the HMDI PCT have values typical for isocyanates reactions: $E = 62.8$ J/g-eqv (in the presence of HBSO) and $E = 52.9$ J/g-eqv (in the presence of CN-DMSO).

The HMDI PCT in the presence of the above mentioned catalysts practically proceeds till complete disappearance of the isocyanate groups and leads to the formation of the highly cross-linked polyisocyanurates. This is confirmed by the

TABLE II

The dependence of composition and molecular-mass parameters of oligoisocyanurates on the conversion degree of CPCT at various ρ_1 (353 K, [HBSO] = 1% by weight)

ρ_1	α	weight parts				total		polym.part	
		HMDI	CHMI	trim.	polym.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.12	0.45	0.29	0.11	0.21	0.39	490	1.85	1300	1.11
	0.57	0.19	0.08	0.16	0.57	690	2.08	1700	1.15
	0.64	0.17	0.05	0.13	0.65	790	2.15	1800	1.19
	0.68		gel-formation						
0.16	0.41	0.32	0.17	0.22	0.29	410	1.82	1210	1.10
	0.52	0.22	0.14	0.18	0.46	520	1.95	1330	1.14
	0.66	0.14	0.10	0.14	0.62	710	2.23	1700	1.21
	0.69		gel-formation						
0.26	0.34	0.30	0.23	0.27	0.20	360	1.62	1120	1.05
	0.40	0.27	0.22	0.26	0.25	370	1.66	1160	1.06
	0.70		gel-formation						
0.40	0.46	0.17	0.26	0.26	0.31	370	1.78	1040	1.11
	0.68	0.05	0.16	0.19	0.60	610	1.99	1360	1.19
	0.84		gel-formation						
0.44	0.37	0.22	0.39	0.26	0.13	280	1.48	900	1.04
	0.62	0.09	0.16	0.27	0.48	520	1.72	1140	1.12
	0.92	0.01	0.03	0.12	0.84	1060	1.72	1550	1.29
	0.98		gel-formation						
0.50	0.23	0.26	0.51	0.20	0.03	230	1.28	820	1.01
	0.44	0.17	0.38	0.27	0.18	290	1.51	880	1.03
	0.64	0.07	0.15	0.31	0.47	440	1.62	960	1.11
	0.86	0.02	0.05	0.25	0.68	650	1.70	1130	1.21
	0.98	0.01	0.02	0.21	0.76	920	1.66	1390	1.26
0.74	0.41	0.13	0.43	0.29	0.15	280	1.31	680	1.05
	0.56	0.08	0.36	0.35	0.21	310	1.32	700	1.04
	0.85	0.01	0.13	0.47	0.39	430	1.28	790	1.05
0.85	0.43	0.07	0.48	0.36	0.08	260	1.22	650	1.02
	0.63	0.02	0.33	0.50	0.14	300	1.21	680	1.02
	0.88	0.01	0.10	0.62	0.27	400	1.15	710	1.04

concentration value of the elastically active chains (or cross-links density) of a polymer network determined by the thermomechanical method[5]: $\nu = 25.4 \times 10^{-4}$ mole/cm^3 (polymer obtained with HBSO) and $\nu = 26.2 \times 10^{-4}$ mole/cm^3 (polymer obtained with CN-DMSO).

One of the ways to decrease the density of a polymeric network and hence to weaken its stressed state and increase the ultimate strength of polyisocyanurates is a copolycyclotrimerization (CPCT) of mono- and diisocyanates. HMDI and CHMI were used as comonomers. The CPCT of isocyanates was carried out in

TABLE III

The monoisocyanate (CHMI) effect on physicomechanical properties of polyisocyanurate networks

ρ_1	Tg,K	$\nu*10^4$ mol/cm^3	compression stress σ, kg/cm^2	compression stress E, kg/cm^2	compression stress ε, %	tension stress σ, kg/cm^2	tension stress E, kg/cm^2	tension stress ε, %
0.00	353	25.0	1400	8690	43.7	290	3615	17.6
0.05	343	9.1	1790	11650	42.7	430	3670	21.3
0.09	309	6.3	2265	14150	51.2	510	3780	26.4
0.13	273	4.9	3970	14620	59.7	450	4380	24.0
0.15	270	3.5	4240	13090	61.2	490	3300	24.6
0.21	268	2.0	5000	12030	69.6	308	3080	28.6
0.34	243	1.3	1420	63	77.0	96	280	155.6
0.40	231	0.6	-	-	-	20	23	175.0

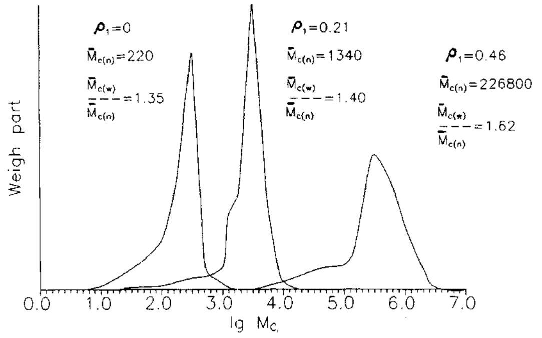


FIGURE 5 The dependence of the molecular-mass distribution of the polyisocyanurate interunit chains on the monoisocyanate content.

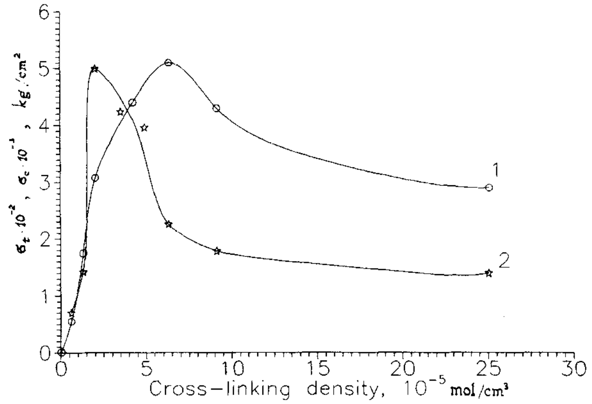


FIGURE 6 The dependence of the hardened polyisocyanurate strength characteristics on the cross-linking density (1 – $\sigma_{tension}$, 2 – $\sigma_{compression}$).

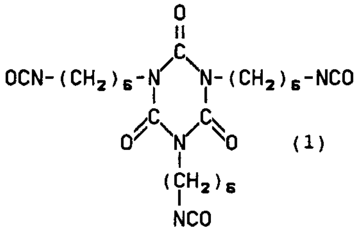
bulk at 353 K and HBSO concentration equal to 1% (by weight). The mole part of NCO-groups of the monoisocyanate in the reaction mixture was varied from $\rho_1 = 0$ (HMDI PCT) up to $\rho_1 = 0.85$.

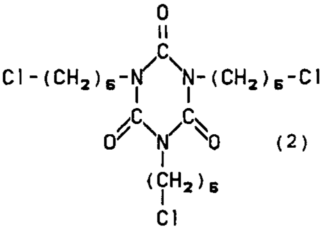
$$\rho_1 = \frac{C_{\mathrm{NCO\ CHMI}}}{C_{\mathrm{NCO\ HMDI}} + C_{\mathrm{NCO\ CHMI}}}$$

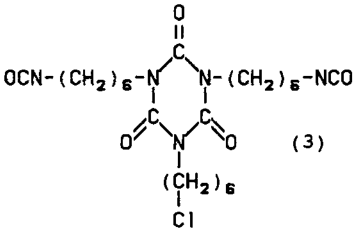
where $C_{\mathrm{NCO\ CHMI}}$ is concentration of the NCO-groups of the CHMI in g-eqv./1, $C_{\mathrm{NCO\ HMDI}}$ corresponds to HMDI.

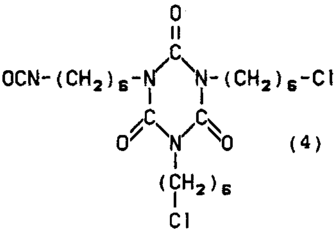
From comparison of kinetic curves of the HMDI PCT, CHMI PCT and CPCT of these isocyanates at various ρ_1 and their anamorphoses in the coordinates of the first order reaction equation follows that all these reactions obey the first order law. Under the identical conditions ($T = 353$ K, 1% by weight HBSO) these reactions have the same rate constants: $k = 2.3 \times 10^{-6} \pm 0.3 \times 10^{-6}\ \mathrm{sec}^{-1}$. This indicates that NCO-groups of the comonomers have the same reactivity.

It can be supposed that in all cases (HMDI PCT, CHMI PCT and CPCT of these monomers) the reaction proceeds through the formation of trimers (1–4) in the initial stages. But in the HMDI PCT and CHMI PCT trimers of type the (1) and (2) are formed accordingly, while in the CPCT the formation of structures of all types (1–4) is possible.


(1)


(2)


(3)


(4)

Indeed, while investigating oligoisocyanurates obtained in the CPCT of mono- and diisocyanates we found in gel-chromatograms the change in location of $V_R^{\max}$ peaks corresponding to trimers as compared with that in the case of the homopolymerization of HMDI and CHMI at the same degree of conversion (Figure 3). Taking into account that molecular masses of trimers (1–4) are rather close we have obtained for the identification of their peaks the relationship V_R (lg $\Sigma\ \Delta V_i$) for the same compounds as in the case of dependence V_R (lg M). $\Sigma\ \Delta V_i$ is the own (Van der Vaals) volume of these compounds which is summarized from increments of Van der Vaals volumes of single atoms.[6]

The comparison of gel-chromatograms of oligoisocyanurates obtained at various

ρ_1 with the calibration dependence shows that the chromatograms have the trimer peaks with $\Sigma\ \Delta V_i$ corresponding to the calculated Van der Vaals volumes of structures (1–4) depending on the content of the initial monoisocyanate. The retention volumes and $\Sigma\ \Delta V_i$ of the trimers (3) and (4) have intermediate values between corresponding ones of structures (1) and (2). However, the insufficient resolution of the trimer peaks does not allow to determine the trimer content exactly. So, in Figure 4 and in Table II summary weight part (w) of the all trimers (1–4) in the reaction mixture are given. It should be noted that the dependences similar to that in Figure 4 at $\rho_1 = 0.5$ were obtained for all ρ_1 investigated. From these results (see Figure 4 and Table II) one may conclude that molecules of monomers and trimers are present in the reaction mixture practically till to the complete CPCT as in the case of the HMDI PCT. From Table II it is seen that the gel-fraction is formed in the system when HMDI predominates in it. At every ρ_1 with increasing α the amount of the high molecular portion increases and the weight part of trimers decreases. In this case the copolymers with molecular masses of the polymer part $\bar{M}_n > 1000$ are formed. When the conversion degree increases the $\bar{M}_n$ value rises up to such degree of conversion at which gel-formation is observed. Experimentally we determined the comonomers ratio when gel does not form in the system. It corresponds to $\rho_1 = 0.5$, i.e. in this case the formation of bi-, mono-, nonfunctional trimers (2–4) takes place with larger probability depending on the amount of monoisocyanate used. At large excess of CHMI ($\rho_1 = 0.74$ and 0.85) the small growth of the high molecular portion with increasing α occurs, its $\bar{M}_n$ is not large and does not almost change with the increase of the conversion degree. The formation of large amount of nonfunctional trimers (2) seems to take place in these cases. They do not take part in further conversion and accumulate in the system.

The polyisocyanurates obtained in the HMDI PCT are highly cross-linked glassy polymers with the corresponding properties—small scission deformation, high module and ultimate strength. Introduction of monoisocyanate in the initial mixture results in decrease of the average degree of cross-linking (ν), in increase of elasticity (ε) at different tests and also in significant changes in ultimate strength of the hardened copolymers (Table III). The glass-transition temperature of the polymer obtained in the CPCT of HMDI and CHMI with close to equimolar ratio is 130° lower as compared that of polyisocyanurate obtained in the HMDI PCT. It indicates the essential change of the topological formation of interunit chains—the appearance of "free ends" of the various topological structures. The average value of cross-linking degree of non-modified polyisocyanurate ($\rho_1 = 0$) shows that inspite of quantitative proceeding of the PCT the formed network structure is far from the ideal one though it has rather narrow molecular-mass distribution of interunit chains at the bimodal distribution function (Figure 5).

The introduction of monoisocyanate in the initial mixture though decreases the topological stress of the resulting polymer but at the same time it contributes the defect of the other type—the appearance of "free ends". This fact leads to extreme dependence of the strength characteristics of the hardened polyisocyanurates on the amount of the monoisocyanate and finally on the cross-linking density of the network (Figure 6).

References

1. A. K. Zhitinkina, N. A. Shibanova and O. G. Tarakanov, "Kinetics and Mechanism of the Isocyanates Catalitic Cyclotrimerization and Polycyclotrimerization," *Uspechi chimii.*, **11**, 1866 (1985).
2. A. L. Smith, "Applied Infrared Spectroscopy", Mir, Moskow (1967).
3. A. I. Kuzaev, "Determination of the Absolute Molecular Masses of the Styrene and Ethylene Oxide Olygomers by the Gel-Permeation Cromatography Method", *Vysokomolek. soed. 22A*, **5**, 1146 (1980).
4. A. I. Kuzaev, "The Terminal Hydroxy Groups Effect on the Retention Volumes in the Gel-Permeation Cromatography", *Vysokomolek. soed. 22B*, **3**, 202 (1980).
5. USSR Patent-1540463 (July 3, 1987). Yu. A. Ol'khov and Ya. I. Estrin.
6. A. A. Askadskiy and Yu. I. Matveev, "Chemical Structure and Physical Properties of the Polymers", Chimiya, Moskow (1983).