Certain Regularities in Three-Dimensional Polycondensation of Oligomeric Compounds

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USSR ACADEMY OF SCIENCES,
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Summary

The authors have studied certain regularities in the three-dimensional polycondensation of oligomeric ether acids with the common formula $C[CH_2OC(O)(CH_2)_nCOOH]_4$, where $n = 2$, 4, 8, with tri- and tetratomic silicoorganic alcohols, various glycols, and diamines. Problems have been considered relating to gel formation in systems containing oligomeric and monomeric branching units. The parameters obtained, which characterize gel formation in oligomeric systems, were compared with the values calculated in conformity with Flory's theory. Research was also carried out on the kinetic regularities of three-dimensional condensations of oligomers, and constants were calculated for the rates of esterifications and the rates of formation of the gel fraction. The thermomechanical properties of polymers were investigated during the condensation processes.

The oligomeric trend in the synthesis of three-dimensional condensation polymers, the basic principles of which were expounded in (1,2-3), has become of late increasingly widespread. Various methods have been suggested for obtaining branched organic and metalloorganic oligomers with functional groups at the branch ends, such as heterofunctional condensation (1,4), transesterification (5,6), step polymerization (7), and hydride relocation (8). As far as the methods of synthesizing polymers from such oligomers are concerned, all research in this field is confined in the main to technological problems typical of each individual class of oligomers. No theoretical investigations related to the specific features of the oligomeric trend in the field of three-dimensional condensation have been undertaken as yet.

TABLE 1

Degree of Reaction Completion, Branching Coefficient at the Point of Polymer Gelation, and Constants of Esterification Rates and the Rates of Gel-Fraction Formation for the Condensation of Tetrafunctional Oligometric Ether Acids with Various Alcohols and Diamines

Kind of condensation (1)	Condensation components (2)	Condensation completion, P_{cr}, % (3)		Branching coefficient, α_{cr} (4)		Rate constants of esterification, K, min^{-1}/(eq/g) (5)	Rate constants of gelation, $K \times 10^2$ min^{-1}/(rel. fr.) (6)
		Found	Acc. to Flory	Found	Acc. to Flory		
$A_4 + B_2$	1. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HOCH$_2$CH$_2$OH	20	57.5	0.04	0.33	1.55	4.87
	2. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$)$_4$OH	25	57.5	0.06	0.33	1.49	3.64
	3. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$CH$_2$O)$_2$H	27	57.5	0.07	0.33	1.42	2.23
	4. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$CH$_2$O)$_3$H	33	57.5	0.10	0.33	0.64	1.87
	5. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$CHO)$_7$H CH$_3$	35	57.5	0.12	0.33	0.44	0.35
	6. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$CH$_2$O)$_x$H m.w. 600	44	57.5	0.19	0.33	0.37	0.25
	7. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2HO(CH$_2$CH$_2$O)$_x$H m.w. 1000	54	57.5	0.29	0.33	0.31	0.20
$A_4 + B_2$	8. C[CH$_2$OC(O)(CH$_2$)$_2$COOH]$_4$ + 2O[SiCH$_2$OCH$_2$CH$_2$OH]$_2$ (CH$_3$, CH$_3$, CH$_3$)	21	57.5	0.04	0.33	1.65	1.36
	9. C[CH$_2$OC(O)(CH$_2$)$_4$COOH]$_4$ + 2O[SiCH$_2$OCH$_2$CH$_2$OH]$_2$ (CH$_3$, CH$_3$, CH$_3$)	40	57.5	0.16	0.33	1.59	0.73
	10. C[CH$_2$OC(O)(CH$_2$)$_8$COOH]$_4$ + 2O[SiCH$_2$OCH$_2$CH$_2$OH]$_2$ (CH$_3$, CH$_3$)	46	57.5	0.21	0.33	1.50	0.65

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	Reaction						
$A_4 + B_2$	11. $C[CH_2OC(O)(CH_2)_4COOH]_4 + 2O[Si(CH_3)_2CH_2NH]_2$	40	57.5	0.16	0.33	—	—
	12. $C[CH_2OC(O)(CH_2)_8COOH]_4 + 2O[Si(CH_3)_2CH_2NH]_2$	45	57.5	0.20	0.33	—	—
$A_4 + B_3$	13. $3C[CH_2OC(O)(CH_2)_2COOH]_4 + 4C_6H_5Si[OSiCH_2OCH_2CH_2OH]_3$	35	41	0.35	0.41	3.02	2.3
	14. $3C[CH_2OC(O)(CH_2)_4COOH]_4 + 4C_6H_5Si[OSiCH_2OCH_2CH_2OH]_3$	36	41	0.36	0.41	1.96	1.9
	15. $3C[CH_2OC(O)(CH_2)_8COOH]_4 + 4C_6H_5Si[OSiCH_2OCH_2CH_2OH]_3$	40	41	0.40	0.41	1.64	1.1
	16. $3C[CH_2OC(O)(CH_2)_4COOH]_4 + 4C_2H_5Si[OSiCH_2OCH_2CH_2OH]_3$	21	41	0.21	0.41	—	2.0
	17. $3C[CH_2OC(O)(CH_2)_8COOH]_4 + 4C_2H_5Si[OSiCH_2OCH_2CH_2OH]_3$	39	41	0.39	0.41	1.67	1.3
$A_4 + B_4$	18. $C[CH_2OC(O)(CH_2)_2COOH]_4 + Si[OSiCH_2OCH_2CH_2OH]_4$	20	33	0.20	0.33	3.49	—
	19. $C[CH_2OC(O)(CH_2)_4COOH]_4 + Si[OSiCH_2OCH_2CH_2OH]_4$	23	33	0.23	0.33	2.58	5.4
	20. $C[CH_2OC(O)(CH_2)_8COOH]_4 + Si[OSiCH_2OCH_2CH_2OH]_4$	24	33	0.24	0.33	1.69	1.5

The most widespread theories of three-dimensional polymeric processes, including the theory of Flory (9), did not consider problems which reflect the influence of the structure and nature of initial compounds on gelatination. However, it was found later, with the aid of statistical analysis of polymeric processes, that the structure of initial monomers, and particularly the degree of symmetry in the arrangement of functional groups in a molecule, affects appreciably the parameters of the gel-formation process (10). Unfortunately, these statistical calculations referred to a particular case and were not confirmed experimentally.

The present work was devoted to the study of certain regularities in three-dimensional polycondensation of branched oligomers, and the influence of the structure and chemical nature of initial oligomeric compounds on the degree of completion of the reaction and the branching coefficient at the moment of polymer gelation. For initial components use was made of oligomeric ether acids (11), having a common formula $C[CH_2OC(O)(CH_2)_nCOOH]_4$, where $n =$ 2, 4, 8, tri- and tetratomic silicoorganic alcohols (12), various glycols, and diamines (13).

The various kinds of three-dimensional condensations of oligomers we have investigated are illustrated in Table 1. In addition to the established values of condensation completion at the point of gelatination P_{cr} and the critical branching coefficient α_{cr}, the table also contains values calculated according to the Flory theory.

The critical completion of condensation was calculated for three-dimensional condensations $A_4 + B_2$, i.e., condensations of tetrafunctional components with difunctional ones, by the formula $P_{cr}^2 = \alpha_{cr}$ (the ratio of various functional groups is equivalent in each condensation), where $\alpha_{cr} = (f-1)^{-1} = 0.33$, with the functionality of the branching unit $f = 4$; for condensations $A_4 + B_4$ by the formula $P_{cr} = \alpha_{cr}$, where $\alpha_{cr} = 0.33$; for condensations $A_4 + B_3$ by the formula $P_{cr} = \alpha_{cr}$, where $\alpha_{cr} = (f_{mean} - 1)^{-1}$; f_{mean} is the arithmetic mean of functionality in the system of tetrafunctional and trifunctional branching units equal to 3.4.

It can be seen when considering the group of type $A_4 + B_2$ condensations that with the constant branching unit—pentaerythritol tetradipate—the completion of condensation at the point of gel formation increases regularly with the growth in the chain of the difunctional component—glycol. The completion of condensation at the point of gelation increased more than twice from the first
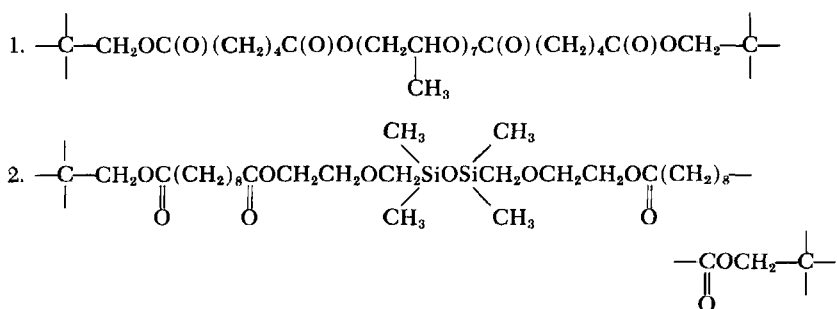
member of the series—ethylene glycol to the last one—polyethylene glycol with a molecular weight of 1000.

The same increase in the completion of condensation at the point of gelation can be observed if, with the same difunctional component, the length of the branch in the ether acid is increased. Thus the minimum completion of the reaction in the series of condensations of bis(oxyethoxymethyl) tetramethyldisiloxane with ether acids (Nos. 8 to 10) was observed in the condensation with tetrasuccinate of pentaerythritol, more in the condensation with tetradipate of pentaerythritol, and the maximun in this series of condensations with tetrasebacinate of pentaerythritol, which had the longest branches.

Study of the type $A_4 + B_3$ and $A_4 + B_4$ condensations confirms the data obtained earlier: With the same constant component of condensation—triatomic or tetratomic silicoorganic alcohol—the degree of reaction completion at the point of gel formation of polymers increases as the branch in the ether acids grows longer.

The effect of the chemical nature of initial components on the completion of reaction at the point of gelation can be traced if we compare the following reactions: (1) condensation of tetradipate of pentaerythritol with heptaisopropyleneglycol (Table 1, Nos. 5 and 2) condensation of tetrasebacinate of pentaerythritol with bis (oxyethoxymethyl) tetramethyldisiloxane (Table 1, No. 10).

When we compare the sections of molecular chain between the points of a three-dimensional framework for these cases,

1. $-\overset{|}{\underset{|}{C}}-CH_2OC(O)(CH_2)_4C(O)O(CH_2CHO)_7C(O)(CH_2)_4C(O)OCH_2-\overset{|}{\underset{|}{C}}-$
$\qquad\qquad\qquad\qquad\qquad\qquad CH_3$

2. $-\overset{|}{\underset{|}{C}}-CH_2O\underset{\underset{O}{\|}}{C}(CH_2)_8\underset{\underset{O}{\|}}{C}OCH_2CH_2O\underset{\underset{CH_3}{/}}{\overset{\overset{CH_3}{\backslash}}{CH_2Si}}OS\underset{\underset{CH_3}{\backslash}}{\overset{\overset{CH_3}{/}}{iCH_2}}OCH_2CH_2O\underset{\underset{O}{\|}}{C}(CH_2)_8-$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad -\underset{\underset{O}{\|}}{C}OCH_2-\overset{|}{\underset{|}{C}}-$

it can be seen that the distance in atoms between two branches is practically the same, the principal difference being the presence of dimethyl-siloxane links in the second case instead of oxyalkylene ones in the polymeric chain 1. This difference in the chemical

nature of polymeric chain is responsible for the fact that in the first case gelation of polymers occurs when the reaction is completed by 35% and in the second when it is completed by 46%.

The same effect of the chemical nature of initial components on on reaction completion at the point of gel formation is quite noticeable when we compare condensations of pentaerythritol tetradipate with diethyleneglycol (No. 3) and with bis(phenylaminomethyl) tetramethyldisiloxane (No. 11). The length of the polymeric chain in the atoms between the framework points for these polymers,

3. —C—CH₂OC(O)(CH₂)₄C(O)O(CH₂CH₂O)₂C(O)(CH₂)₄C(O)OCH₂—C—

4. —C—CH₂OC(CH₂)₄C—N—CH₂SiOSiCH₂—N—C(CH₂)₄COCH₂—C—
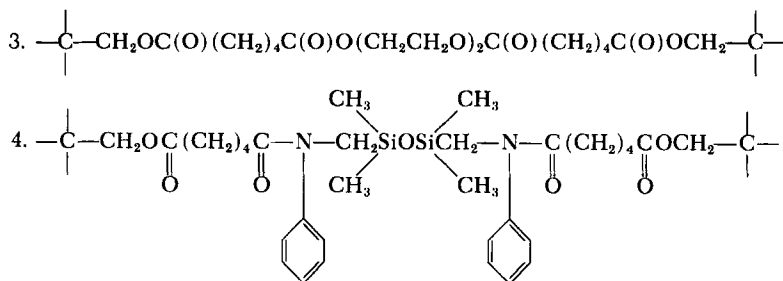
is the same, but the difference in the chemical composition of polymers causes the polyetheramidosiloxane polymers to reach the point of gelation at $P_{cr} = 40\%$ and the polyethers at $P_{cr} = 27\%$.
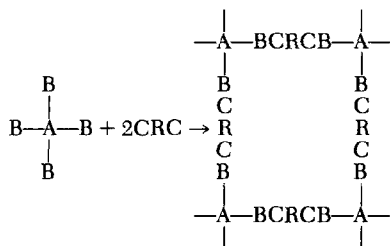
These regularities in the change in reaction completion at the point of gelation can be attributed to the specific features in the structure of polymers being formed. It is known that the process of gel formation in polymeric systems develops gradually, from the initial insignificant quantities of nonfusible and unsoluble polymer at the point of gelation to a high degree of transformation of the polymeric system into gel. It is often extremely difficult to determine the point of gelation by sight. In the course of the reaction the polymeric system is still quite fluid, but at the same time it contains the first amounts of gel fraction which can be identified in the form of microgels, for example, when the properties of such polymers are investigated in solutions. One can naturally expect that the formation of the first amounts of microgels in polymeric systems (point of gelation) depends, first, on the nature of the three-dimensional structure being formed and, second, on its chemical nature. The more loose and flexible these arising three-dimensional structures, the better they will dissolve and the greater degree of condensation

is required to complicate this structure and convert it into an un-soluble and nonfusible gel.

From this point of view, and depicting schematically the three-dimensional condensation (type $A_4 + B_2$) as

$$
\begin{array}{ccc}
 & \overset{|}{-A}-BCRCB-\overset{|}{A}- & \\
B & B & B \\
| & C & C \\
B-\overset{|}{A}-B + 2CRC \rightarrow & R & R \\
| & C & C \\
B & B & B \\
 & \underset{|}{-A}-BCRCB-\underset{|}{A}- &
\end{array}
$$

the results obtained can be formulated as follows:

1. An increase in the size of an elementary cell of a polymeric framework for one homologous series of polymers, or (what is the same) an increase in the length of the chain between the points of framework AA makes this structure more flexible and retards the moment of precipitation of gel fraction in favor of more complex three-dimensional structures, i.e., promoting thereby the comple-tion of the reaction.

2. Depending on the chemical nature, the polymeric chain AA between the framework points will be characterized by various degrees of flexibility and flowability. The more elastic such a chain is, the smaller will be the value of polymer segment that corre-sponds to it and the more complex should be such a structure to make possible conversion of this polymer into gel, and the greater completion of reaction should be attained at the point of gelation.

The degree of reaction completion at the point of gelation also depends on the number of additional points formed by interlacing of the chains (Fig. 1). When the polymeric chain AA between the framework points is not large, a greater number of effective bonds may arise, owing to chain interlacing in the same volume of a poly-mer, which may cause the gel to form at a smaller degree of reaction completion. When the elementary cell of the framework, i.e., the chain AA (Fig. 1), is increased, the interlacing chains are liable to slide over large distances. This makes the formation of additional points in the same polymeric volume less probable, and a greater

degree of reaction completion is required to reach the point of gelation.

It follows, therefore, that the established increase in the completion of condensation at the moment of gel formation and the growth in the critical branching coefficient due to larger chains of glycols or
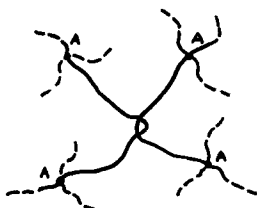

FIG. 1. Formation of a point in a polymeric framework due to the interlacing of chains.

branches in ether acids can also be attributed to the different number of additional points produced by the interlacing of chains.

If we compare data describing the degree of completion of three-dimensional condensations and branching coefficients of monomeric systems with the data obtained for oligomers, we shall not fail to see that in the majority of cases oligomeric systems reach the point of gelation at a much lesser degree of transformation of functional groups. For example, the data we have obtained show that the system of monomers

1. $C(CH_2OH)_4 + 4HOOC(CH_2)_4COOH + 2HOCH_2CH_2OH$

reaches the point of gelation at $P_{cr} = 63$ to 64% and $\alpha = 0.39$, which differs but little from the experimental data Flory obtained for identical systems. The oligomeric system of the same composition,

2. $C[CH_2OC(O)(CH_2)_4COOH]_4 + 2HOCH_2CH_2OH$

reaches the point of gelation at $P_{cr} = 20\%$ and $\alpha_{cr} = 0.04$. This seems at first sight to contradict the conclusions outlined above, since in the case of monomer condensation the elementary cell of the framework should be the smallest. With a high degree of conversion of polymers into gel, the distance between the points of a three-dimensional framework for monomeric systems is in all probability smaller than for oligomeric ones. However, the arising three-dimensional structures should differ considerably at the point of gelation, owing to a different structure of monomeric and oligomeric

branching units, which is proved by the various degree of condensation. At the point of gel formation, and to a lesser degree of polymerization the oligomeric systems, are apparently more developed in three-dimensional direction, while monomeric systems at a larger degree of polymerization are branched off less. Thus, in the polymeric chain of the above-described monomeric system 1,

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
| \\
-\text{OCH}_2\text{CH}_2\text{OC(O)(CH}_2)_4\text{C(O)OCH}_2\text{—C—CH}_2\text{OC(O)(CH}_2)_4\text{C(O)—} \\
| \\
\text{CH}_2\text{OH}
\end{array}
$$
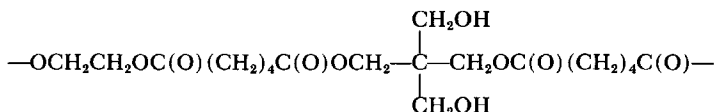
the hydroxyl of the branching unit is positioned at a distance of only one atom from the branching center. The movement of this hydroxyl is limited, being dependent on the flexibility and flowability of the basic polymeric chain. In the oligomeric system 2 and in the same polymeric system,

$$
\begin{array}{c}
\text{CH}_2\text{OC(O)(CH}_2)_4\text{COOH} \\
| \\
-\text{OCH}_2\text{CH}_2\text{OC(O)(CH}_2)_4\text{C(O)OCH}_2\text{—C—CH}_2\text{OC(O)(CH}_2)_4\text{C(O)—} \\
| \\
\text{CH}_2\text{OC(O)(CH}_2)_4\text{COOH}
\end{array}
$$
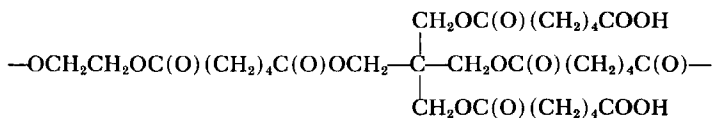
the functional carboxyl of the branching unit is at the end of a flexible and movable branch. The mobility of this carboxyl depends to a much lesser degree on the mobility of the basic chain. For this reason, in the case of condensation of oligomeric compounds, the interchain cross-linking and development of the structure in three directions should proceed much more easily. Hence oligomeric systems are lighter, and, at a smaller degree of transformation of functional groups, can reach the three-dimensional structural forms which precipitate into gel. This explains, apparently, the jumpy change in the parameters of gel formation observed during transition from monomeric branching units to oligomeric ones.

Comparison of the established parameters of oligomer gelation with the identical parameters calculated according to the Flory theory (Table 1) leads us to the conclusion that the theory (Flory) three-dimensional polymeric processes cannot be applied to condensation oligomeric systems. According to the data the Flory theory is also at variance with the experimental data for monomeric polymerizing systems (14). A number of works devoted to the study of condensation monomeric systems point out similar discrepancies (15,16). These differences can be apparently explained by a purely

statistical character of analysis of three-dimensional processes in the Flory theory, which disregarded the influence of such important factors as the structure and chemical nature of initial components as well as the structural forms of polymers at the point of gelation.

The kinetic regularities of three-dimensional condensations of oligomers to the point of gelation were studied with the aid of functional analysis of polymers and viscosimetric investigations. After the point of gelation of polymers, the control of the reactions was studied by the yield of gel fraction, by means of the functional analysis of polymers using infrared spectroscopy, by the analysis of the soluble fraction, and by the analysis of the changes in the thermomechanical properties of polymers.

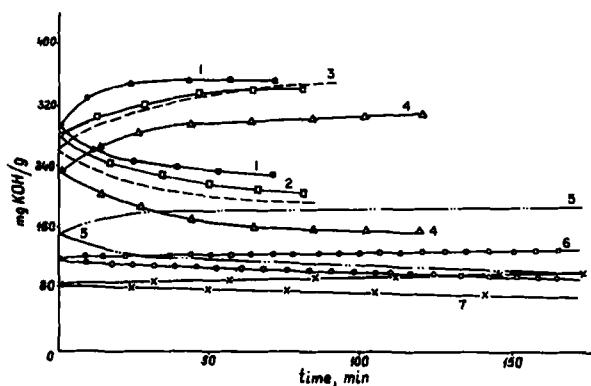Figure 2 shows the change in the acid and ester numbers of poly-

FIG. 2. Change in the acid number (lower branches of parabolas) and ester number (upper branches) in the process of condensation of pentaerythritol tetradipate with ethyleneglycol (1), butyleneglycol (2), diethyleneglycol (3), triethyleneglycol (4), heptaisopropyleneglycol (5) (part of the curve), and polyethyleneglycols (6) and (7) with molecular weights of 600 and 1000 (parts of the curves).

mers up to the point of gelation in the homologous series of condensation of pentaerythritol tetradipate with glycols. As can be seen, an increase in the length of glycol chains reduces the reaction rate, which is proved by a smaller curvature of the parabolas. The data of our experiments show that for all investigated types of three-dimensional condensations, the rate of esterification before and after the point of gelation of polymers decreases with longer branches in the oligomeric ether acids and longer chains between the functional groups in other components, or (what is the same)

with a reduced initial concentration of functional groups. Analysis of the data on ester and acid numbers and on the yield of the gel fraction has shown that reactions of the second order (analytical and graphical methods) correspond to the condensation. The calculated values of the constants of oligomer condensation rates up to the point of gelation as well as of the constants of formation rates for the gel fraction are illustrated in Table 1.

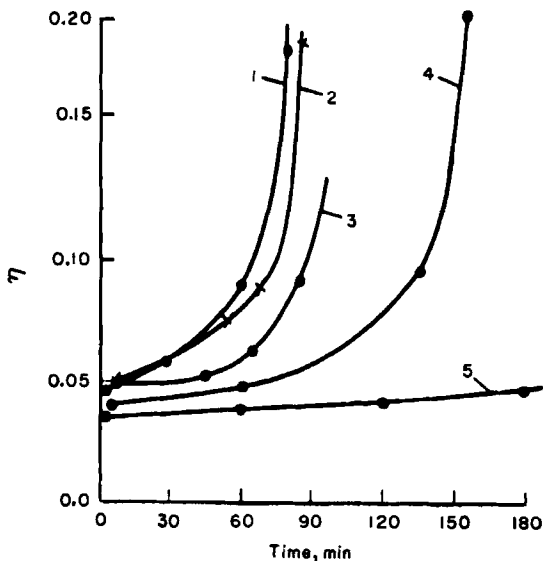Figure 3 shows the change in the specific viscosity of the reaction

FIG. 3. Change in the specific viscosity of the products in the course of condensation of pentaerythritol tetradipate with ethyleneglycol (1), butyleneglycol (2), diethyleneglycol (3), triethyleneglycol (4), and heptaisopropyleneglycol (5) (part of the curve).

products in the same homologous series of condensations. In all the cases, viscosity increases at the beginning of condensation very slowly and sharply as the point of gelation is being reached. This is a very typical feature of three-dimensional condensation.

The kinetics of condensation of pentaerythritol tetradipate with glycols in terms of increase in the gel-fraction is illustrated in Fig. 4. The change in the rates of formation of the gel fraction in various condensations of the same homologous series takes the same regular course as the changes in the rate of esterification up to the point of gelation.
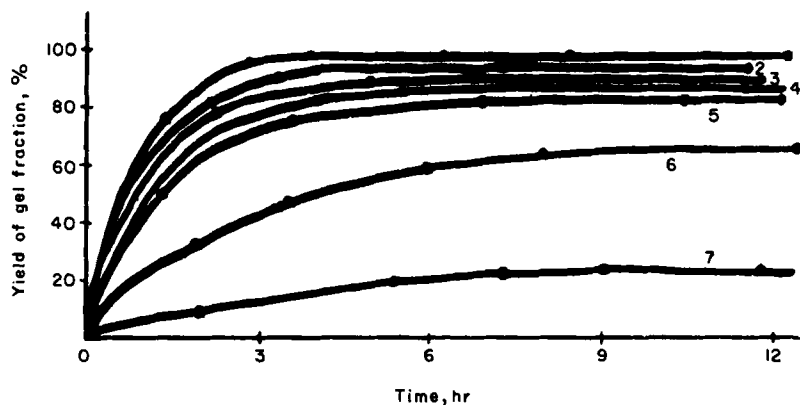
FIG. 4. Yield of gel fraction in the process of condensation of pentaerythritol tetradipate with ethyleneglycol (1), butyleneglycol (2), diethyleneglycol (3), triethyleneglycol (4), heptaisopropyleneglycol (5), and polyethyleneglycols (6) and (7) with molecular weights of 600 and 1000.

The functional analysis of polymeric systems after the point of gelation, carried out with the aid of infrared spectroscopy, has shown that the content of functional groups in the system continues to decrease. However, it proved impossible to assess the degree of conversion quantitatively.

The results of investigation of the thermomechanical properties of polymers during the various stages of the reaction are represented in Fig. 5, using, as an example, the condensation of tetradipate of pentaerythritol with tetra(oxyethoxymethyldimethylsiloxy)silane. The data show that three-dimensional condensation passes through a number of consecutive stages. The first stage, with a relatively low degree of reaction completion, produces soluble products, for which the dependence of deformation on temperature takes the form of a curve typical of low-molecular liquids liable to vitrify (Fig. 5, curve 1). As condensation proceeds further, when the framed structure of the polymer is not yet adequately developed, it is possible to trace in certain cases the appearance of a region of highly flexible deformation. Further development of three-dimensional structure engenders brittleness in the polymers and results in products wholly devoid of the region of highly flexible deformation. It can be seen in the figure that the development of a framed structure gradually decreases the defor-
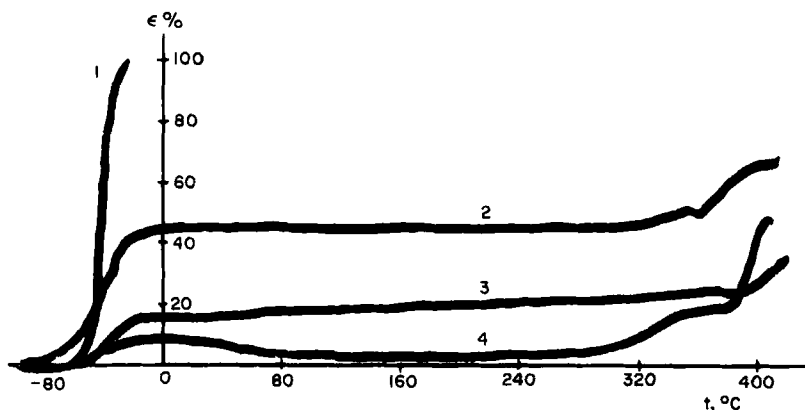
FIG. 5. Thermomechanical curves of the products of condensation of tetrakis (oxyethoxymethyldimethylsiloxy) silane with tetradipate of pentaerythritol during various stages. Polymers with the reaction completion (by COOH) by 20% (1), polymers containing 20% of gel fraction (2), 73% of gel fraction (3), and 90% of gel fraction (4).

mation of polymers from 50% (curve 2) to 2 to 3% (curve 4). Deformation above 350°C initiates polymer destruction.

EXPERIMENT

Three-dimensional polycondensations of oligomeric ether acids with glycols, silicoorganic alcohols, and diamines were conducted with the aid of the methods described below. In all the cases, the initial amounts of reagent conformed to the equivalent ratio of the reaction groups. All condensations took place in the same conditions: at 160°C in the flow of dry nitrogen and a melt of the components.

Condensation of pentaerythritol tetradipate 14.19 g (0.021 mole) with heptaisopropyleneglycol 18.39 g (0.042 mole) was performed at 160°C in a flask provided with a stirrer, thermometer, straight-reflux condenser, and an inlet for passing nitrogen. After homogenization of the mixture (about 1 min), samples were taken from the flask after definite and increasing time intervals, while continuing to stir the mixture to determine the viscosity and the degree of condensation completion (by the drop in the acid number and increase in the ester number). The samples were dissolved in ethyl alcohol or in a 1:1 mixture of alcohol and toluene. For titration,

0.05 N solutions of HCl and KOH in alcohol were used. The data obtained are represented in Figs. 2 and 3. The point of gelation was determined by the moment when the condensation products ceased to dissolve in boiling solvents. After the point of gelation, stirring was ceased and condensation continued under the same conditions. An increase in the gel fraction in the system was periodically controlled. Each sample was extracted with absolute ethyl alcohol in a Soxhlet device with a maximum working volume of 30 cm³. After extraction, the gel was dried to constant weight at a temperature of 80°C in vacuum and the extracted soluble fraction was checked for the acid and ester numbers. The acid numbers of the soluble fraction in the course of condensation and after the point of gelation are as follows (in mg KOH/g): 93(40 min), 91(1 hr, 20 min), 91(2 hr, 40 min), 95(4 hr, 40 min), 98(20 hr, 40 min). The yield of gel fraction in time is illustrated in Fig. 4.

The elementary composition of the reaction mixture is: directly after homogenizing, C 54.66%, H 8.77%; at the point of gelation, C 56.01%, H 8.68%; and with complete gelation, C 57.13%, H 8.24%.

CONCLUSIONS

1. It has been found in investigating three types of three-dimensional condensation of oligomeric ether acids with various di-, tri-, and tetrafunctional compounds that at the point of polymer gelation the completion of reaction and the branching coefficient depend on the structure and chemical nature of the initial components.

2. An increase in the size of the elementary cell of a three-dimensional polymeric framework, which may be caused by any condensation component, increases the degree of reaction completion at the point of gelation for one homologous series of polymers. Such changes can be attributed to a heightened flexibility of polymeric chains and a smaller probability of formation of additional points due to the interlacing of the chains.

3. As distinct from monomeric condensation systems, the investigated oligomeric systems reach the point of gelation at a much smaller degree of conversion of functional groups and a lower value of the branching coefficient, which can be explained by an easier attainment of the three-dimensional polymeric forms, which precipitate into gel, in the reactions of branched oligomers.

4. The established values of parameters which characterize gel formation in the three-dimensional systems of oligomers do not correspond to those calculated according to the theory of three-dimensional processes by Flory. These contradictions can be obviously attributed to the purely statistical nature of analysis employed in Flory's theory, which disregards such factors as the structure and chemical nature of the initial components of the reaction and the structural forms of the polymer at the point of gelation.

5. We have studied certain kinetic regularities of three-dimensional condensations of oligomers and calculated the constants of esterification rates and the constants of the rates of gel-fraction formation. In the course of condensations we have investigated the thermomechanical properties of polymers.

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Zusammenfassung

Untersucht wurden gewisse Gesetzmässigkeiten in der dreidimensionalen Polykondensation von oligomeren Äthersäuren der allgemeinen Formel $C[CH_2OC(O)(CH_2)_nCOOH]_4$, wobei $n = 2$, 4, 8, mit drei- und vieratomigen silicoorganischen Alkoholen, verschiedenen Glykolen, und Diaminen. Die Problmatik in Bezug auf die Gelbildung in Systemen mit

oligomeren und monomeren Verzweigungsgruppen wurde untersucht. Die erhaltenen Parameter, die die Gelbildung in oligomeren Systemen charakterisieren, werden mit den nach der Flory'schen Theorie berechneten Werten verglichen. Ebenfalls untersucht wurden die kinetischen Gesetzmässigkeiten der dreidimensionalen Kondensation von Oligomeren. Hierbei wurden Konstanten für die Geschwindigkeit der Esterifizierung und der Bildung der Gelfraktion bestimmt. Die thermomechanischen Eigenschaften der Polymeren während des Kondensationsprozesses wurden untersucht.

Résumé

Les auteurs ont etudié certaines regularités dans la polycondensation tridimensionnelle des étheracides oliqomériques d'une formule commune $C[CH_2OC(O)(CH_2)_nCOOH]_4$, où $n = 2, 4, 8$, avec des alcools organosiliciés tri-et tétraatomiques, avec des glycols variés, et des diamines. On a consideré les difficultés associées avec la formation des gels dans des systèmes contenant des unités ramifiées oligomères et monomères. On a comparé les paramètres obtenues, caracterisant la formation de gels dans des systèmes oligomères avec des valeurs calculées en accord avec la théorie de Flory. On a également fait des recherches sur les regularités cinétiques de la condensation tridimensionnelle des oligomères et des constantes calculées pour les vitesses d'esterification et les vitesses de la formation des fraction-gels. On a etudié les proprietés thermoméchaniques des polymères pendant les procedés de condensation.