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Polymethacrylate Networks: Thermodynamics and Kinetics of Thermal Degradation

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Several types of oligoesteracrylates are synthesized and the crosslinked polymers obtained from these oligomers subjected to thermal decomposition. A detailed study of thermodynamics and kinetics of degradation of these network polymers is presented.

KEY WORDS Oligoesteracrylates, networks, thermal degradation, thermodynamics, kinetics.

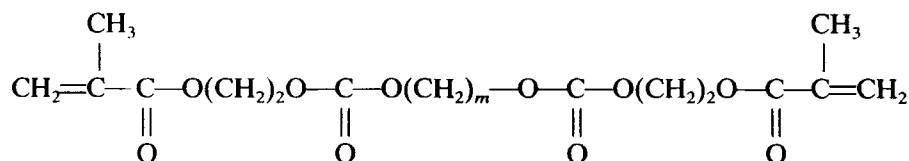
1. INTRODUCTION

Oligoesteracrylates (OEA) represent a wide field of polyreactive compounds with methacrylate endgroups and a regular arrangement of methacrylates groups. The methods of OEA synthesis have been first elaborated in USSR by A. A. Berlin.^{1–4} By changing the chemical nature and the dimension of the oligomer blocks, the order of location, and the types of reactive groups, one can purposefully influence the structure and properties of oligomer liquid and of cross-linked polymers derived from it.

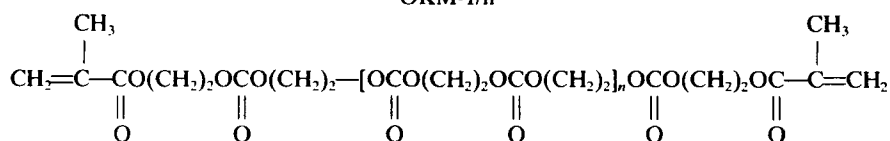
It should be noted that OEAs open new possibilities for the technology of polymers and materials for production of large-size articles from sufficiently thermostable polymer materials with high strength.

OEAs are used as constructive materials, electroisolating compounds, hermetic substances working in wide temperature ranges, aircraft and rocket components, radio equipment, material for ships, medical instruments etc.^{5–8}

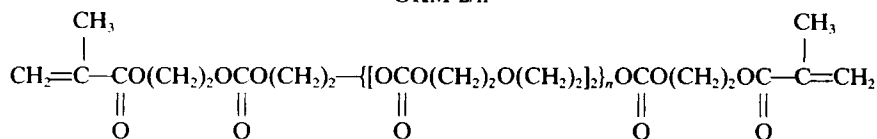
The OEA polymers of homologous series: dimethacrylate esters of *n*-alkylene-glycols (DAG: ME-MD), oxyalkylene-glycols (DOG: TGM-3,-13), diethylene-glycolephthalates (MDPh), oligocarbonate-methacrylates based on oxyalkylene-glycols (OKM-*m/n*) and alkylene-glycols (OKM-*n*) have been the main objects of the present investigation.

OKM- m/n 

where $n = 1$ ($m = 2$); 9 ($m = 4$); 10 ($m = 6$), and oligomers with the repeating carbonate groups:

OKM- $1/n$ 

where $n = 0, 1, 2, 3, 4, \dots$

OKM- $2/n$ 

where $n = 0, 1, 2, 3, 4, \dots$

OKMs were synthesized by the method of condensation telomerization in conditions of nonequilibrium low temperature polycondensation. They represent systems with narrow molecular mass distribution (MMD). Process of OEA polymerization was carried out in presence of radical initiators (benzoyl peroxide, azobis-isobutyronitrile etc.).^{19,25}

The extent of OEA polymerization was evaluated by the change of absorption C=C bonds at 1636 cm^{-1} in the IR spectrum of this material, as well as by reactions of Br and O_3 with unsaturated double bonds.^{9,10}

It has been shown previously,¹¹⁻¹⁵ that OEA polymers are characterized by a microheterogeneous globular structure.

Physical properties of three-dimensional polymer structure depend on chemical nature of OEA and conditions of polymer formation. The polymerization process of OEA in liquid-crystalline state results in formation of network polymer with crystalline structure.^{2,16}

2. CHARACTERISTICS OF POLYMETHACRYLATE NETWORK PYROLYSIS

Thermogravimetric (TG and DTG) analysis of polymers in inert atmosphere was carried out using a Stanton Redcroft TG-750 instrument.

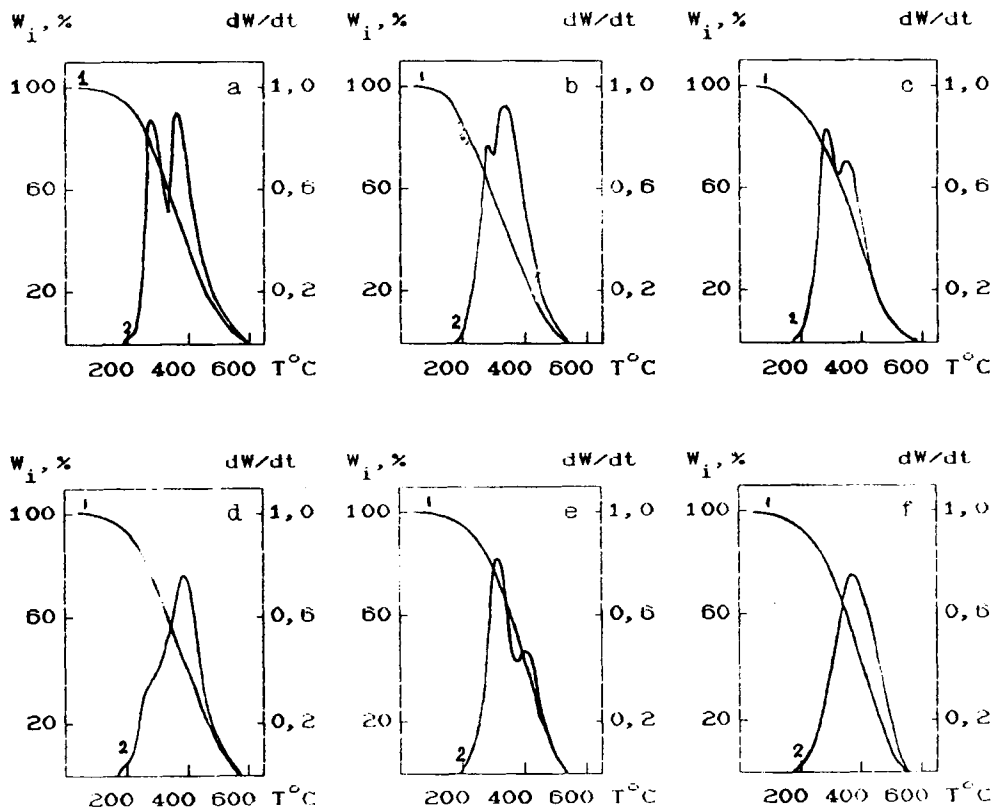


FIGURE 1 Thermogravimetric curves, TG, (1) and rates of thermal degradation, DTG, (2) for net polymethacrylates: ME (a), MB (b), TGM-3 (c), MDPH-2 (d), OKM=1/2 (e), OKM-2/1 (f), heating rate is 10 deg./min., (Helium).

For the case of network OEA-polymer pyrolysis under dynamic heating conditions (0.8–20°C/min) (Figure 1),^{17–20} the presence of two stages of degradation differing in kinetics and mechanism was noted.

The temperature interval of these stages depends on the nature of initial OEA and the heating rates. The characteristic temperatures for polymer's degradation are displaced to the high-temperature region by increases of the heating rate.

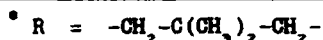
During the first stage ($T < 250\text{--}300^\circ\text{C}$) the polymers DAG, DOG, MDPH, OKM-n etc. decompose with the yield of OEA monomers. This result was confirmed by the methods of liquid and gas chromatography (HPLC, GC), IR- and NMR-spectroscopy, mass-spectroscopy.^{17–25}

Thus at moderate temperatures, 250–300°C, the network polymethacrylates decompose like linear PMMA by the mechanism of depolymerization. At the second stage (at temperatures higher than 300°C) the depolymerization process takes place as well as the scission of side bonds in polymer structure. This process leads to a mixture of decomposition products (liquid and gaseous) including the initial oligomers (Table I).

TABLE I

The effective kinetic parameters of net OEA polymers thermal degradation

Net OEA polymers	Polymerizat. depth, P, %	Cross-linking degree, ϵ	T_{id}^1/T_{max}^1 , °C	E_{eff}^1 kJ/mole	n_{eff}^1	E_{eff}^2 kJ/Mole	n_{eff}^2
ME	68,0	0,36	243/350	105,4	1,5	153,7	1,8
MB	74,0	0,43	235/349	100,0	1,6	172,2	1,7
MC	83,0	0,66	226/342	99,1	1,5	166,3	1,8
MD	81,5	0,63	216/330	95,8	1,0	235,2	2,0
TCM-3	78,4	0,57	250/315	166,0	1,0	201,0	2,0
MDPh-2	96,0	0,92	200/280	132,0	1,0	156,5	1,0
OKM-1/0	98-99	0,98	243/347	104,5	1,8	211,5	1,4
OKM-1/2	--	--	233/298	98,7	1,6	184,7	2,2
OKM-1/3	--	--	230/284	93,6	1,5	194,8	2,4
OKM-1/4	--	--	234/289	96,1	1,6	200,6	2,0
OKM-2/0	--	--	245/302	107,4	1,6	213,6	2,0
OKM-2/1	--	--	252/355	127,0	1,2	-	-
OKM-2/2	--	--	239/360	124,1	1,7	-	-
OKM-2/3	--	--	250/370	125,8	2,0	-	-
OKM-2/4	--	--	258/377	129,8	1,6	-	-
OKM-9	--	--	243/358	102,0	2,0	282,0	2,0
OKM-10	--	--	240/355	100,3	1,4	300,9	1,2
OKM-11*	75	0,50	245/305	105,0	1,4	200,0	1,6



T_{id}^1 is the initial temperature of polymer decompose at the first stage, T_{max}^1 is the temperature corresponding to maximal rate of destruction (DTG) at the first stage, E_{eff}^1 and E_{eff}^2 are effective activation energies at the first and second stages, n_{eff}^1 and n_{eff}^2 are effective orders of the degradation process at the first and second stages.

The yield of OEA (monomer) in the case of network polymethacrylates thermal degradation decreases on increases of temperature and molecular mass of the initial dimethacrylate (Figure 2).^{19,24,25}

More severe heat treatment leads to deep fragmentation of OEA polymers. A comparative analysis of total yield of low-molecular decomposition products of OEA and their network polymers [under constant heating rate (300–800°C)] (Figure 3) shows a decrease of thermal stability of polymers and of initial OEA monomers in a homologous series. It should be noted that the extent of the secondary process of network polymer pyrolysis depends on the initial OEA molecular mass and volatility of OEA.

High-temperature pyrolysis of OEA polymers includes scission reactions of ester bonds via intermolecular mechanism involving *cis*-elimination of hydrogen as well as radical reactions of C—O bonds breaking in α , β , γ -positions with respect to carbon atom from carbonyl group.^{21,25}

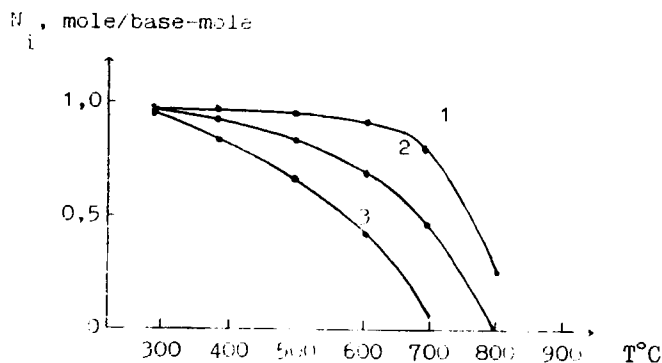


FIGURE 2 Temperature influence on the yield of monomers during the pyrolysis of polymers: (1)—PMMA, (2)—PME, (3)—PMD.

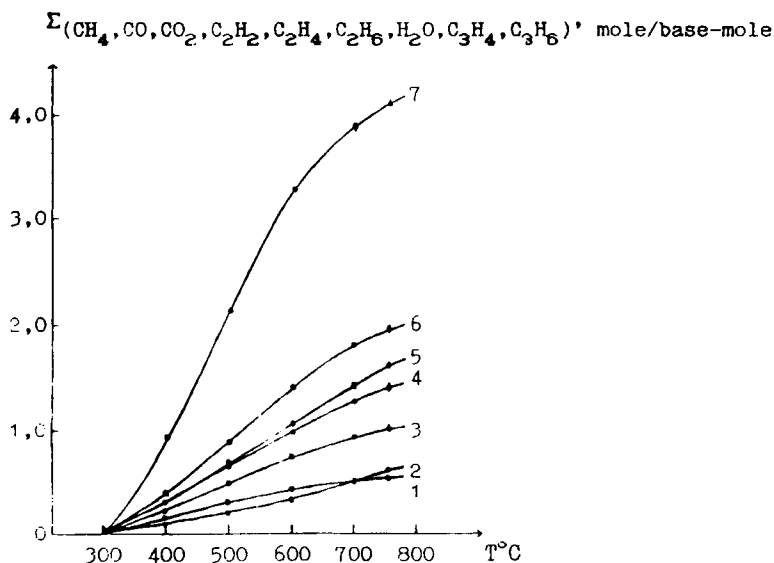


FIGURE 3 Temperature dependence of total yield of low-molecular products of monomer and polymer degradation. 1—ME, 2—PMMA, 3—PME, 4—MD, 5—PMD, 6—OKM-1/0, 7—polymer of OKH-1/0.

3. THERMODYNAMIC PARAMETERS OF PYROLYTIC REACTIONS OF OLIGOESTERACRYLATES

The thermodynamic parameters of OEA and their polymers are necessary for determination of polymers thermal stability and prediction of direction for pyrolytic reactions.

The enthalpy of formation (ΔH_f^0) and free energy of formation (ΔG_f^0) of investigated compounds can be calculated by the method of Franklin and Souders.^{26,27}

The free energy function, $\Delta G_f^0 = f(T)$, is calculated as sum of simple increments and additional terms for molecular symmetry— $RT \ln \sigma$, where σ is the symmetry

factor for the carbon skeleton of the molecule. The OEA entropy of formation (S_f^0) is calculated using the statistical data. It can be represented as a sum of contributions: $S_{tr.}^0$ = translation entropy, $S_{vib.}^0$ = vibration entropy, $S_{rot.}^0$ = external rotation entropy, $S_{in.rot.}^0$ = internal rotation entropy:

$$S_f^0 = S_{tr.}^0 + S_{rot.}^0 + S_{in.rot.}^0 + S_{vib.}^0$$

The calculation of individual entropy contributions is based on orthographic projections for the first member in OEA homologous series which is constructed using the IR spectroscopy data.²⁶

The additive quality of entropy function was taken into account in the calculations for other members of the homologous series.

The values of standard OEA enthalpy formation for some homologous series are listed in Table II.

The OEA free energy data calculated at 298–1000°K allow one to represent the functional dependencies for homologous series of OEA – $\Delta G_f^0 = f(T, n)$, kJ/mole, where T is temperature (°K) and n is a number of repeating groups in homologous series of OEA.

For DAG series:

$$\Delta G_f^0 = [0.79 + 0.08(n - 2)]T - [665.00 + 16.7(n - 2)], \text{ kJ/mole}$$

$$n = 2, 3, 4 \dots$$

DOA series:

$$\Delta G_f^0 = [1.00 + 0.30(n - 1)]T - [815.00 + 133.0(n - 1)], \text{ kJ/mole}$$

$$n = 1, 2, 3 \dots$$

MDPh series:

$$\Delta G_f^0 = [1.88 + 0.96(n - 1)]T - [1567.0 + 756.0(n - 1)], \text{ kJ/mole}$$

$$n = 1, 2, 3 \dots$$

OKM-n series:

$$\Delta G_f^0 = [1.67 + 0.17(n - 2)]T - [1538.0 + 38.4(n - 2)], \text{ kJ/mole}$$

$$n = 2, 3, \dots$$

OKM with repeating $[\text{OCH}_2\text{CH}_2\text{OC}]_n$ -chain series:



TABLE II
Standard OEA enthalpies of formation

OEA	$-\Delta H_f^{298}$, kJ/mole
<p style="text-align: center;">DAG</p> $\text{CH}_2=\text{C}(\text{CH}_3)\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2)_n-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_3)=\text{CH}_2$ <p>(ME) - n=2 (MB) - n=3 (MB) - n=4 (MG) - n=5 (MG) - n=6 n=7 n=8 n=9 (MD) - n=10</p>	<p>652 673 694 715 736 757 778 798 818</p>
<p style="text-align: center;">DOG</p> $\text{CH}_2=\text{C}(\text{CH}_3)\overset{\text{O}}{\parallel}\text{C}-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_3)=\text{CH}_2$ <p>n=2 n=3 - (TGM-3) n=4 n=5</p>	<p>808 901 1153 1271</p>
<p style="text-align: center;">MDPh</p> $\text{CH}_2=\text{C}(\text{CH}_3)\overset{\text{O}}{\parallel}\text{C}-[\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}]_n-$ $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_2-\overset{\text{O}}{\parallel}\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ <p>n=1 n=2 n=3</p>	<p>1500 2313 3008</p>
<p style="text-align: center;">OKM</p> <p>OKM-1 OKM-2/0</p>	<p>1808 1963</p>

$$\Delta G_f^0 = [1.67 + 0.17(n - 2)]T - [1538.0 + 418.0(n - 2)], \text{ kJ/mole}$$

$$n = 2, 3, 4 \dots$$

The free energy of OEA formation dependencies allow us to evaluate the comparative thermodynamic stability of different OEA. The criterion of thermodynamic stability ($T_{cr.}$) can be defined as:

$$\Delta G_f^0 = \Delta H_f^0 - T_{cr.} \Delta S_f^0 = 0: \quad T_{cr.} = \Delta H_f^0 / \Delta S_f^0$$

The dependence for critical temperatures of OEA on the number of repeating groups in homologous series is shown in Figure 4. It is important to note that different trends (increases or decreases) of T_{cr} exist in the series. This phenomenon was satisfactorily explained by different contributions of enthalpy and entropy in Gibbs energy of formation OEA. For this reason we statistically calculated the S_f^0 as sum of S_{tr}^0 , S_{rot}^0 , $S_{in.rot}^0$, S_{vib}^0 for DAG ($n = 1$) and MDPH ($n = 1$) (Figure 5a,b).²⁶

The decrease of thermodynamical stability for DAG series with increase of CH_2 groups depends primarily on entropy factors. On the other hand, the increase of MDPH thermodynamic stability depends on enthalpy factors. Similar results were obtained also with other OEA series.²⁷

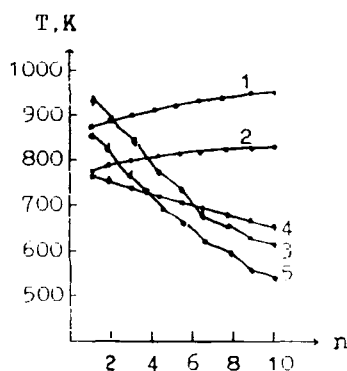


FIGURE 4 Dependence of critical temperatures (T_{cr}) on number of repeating groups (n) in homologue series: 1—OKM with repeating $-\text{OCH}_2\text{CH}_2\text{OC}-$ section, 2—MDPh, 3—OKM- n , 4—DOG, 5—DAG.

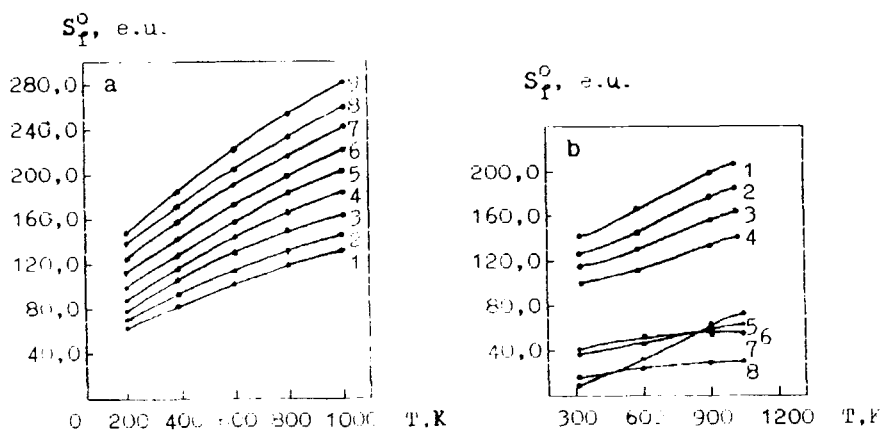


FIGURE 5 Temperature dependence of entropy of formation (S_f^0) for DAG-(a) with: 1— $n = 2$, 2— $n = 3$, 3— $n = 4$, 4— $n = 5$, 5— $n = 6$, 6— $n = 7$, 7— $n = 8$, 8— $n = 9$, 9— $n = 10$; MDPH-(b): 1— $n = 4$, 2— $n = 3$, 3— $n = 2$, 4— $n = 1$, 5— S_{vib}^0 , 6— S_{rot}^0 , 7— S_{tr}^0 , 8— $S_{in.rot}^0$.

4. HIGH TEMPERATURE DEGRADATION OF NETWORK POLYMERS BASED ON OLIGOESTERACRYLATES (OLIGOCARBONATE-METHACRYLATES)

Thermodynamic examination of pyrolysis of OEA, containing carboxylate and carbonate groups, allows us to predict the probability of pyrolysis of OEA and polymers based on OEA.

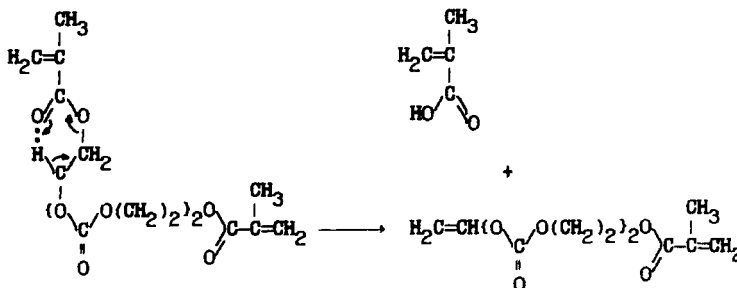
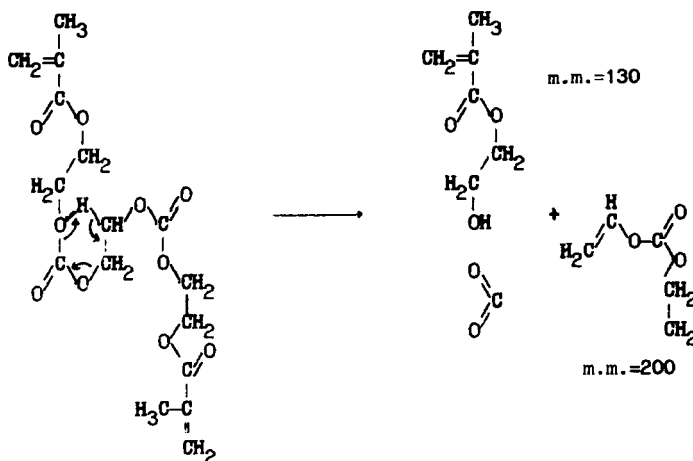
For this reason, the Gibbs energies of OEA scission reactions were calculated using Franklin and Souders methods in the temperature range between 298–1000°K.^{21,25} These calculations were based on the values of OEA free energy of formation and free energy of formation of assumed reaction products.

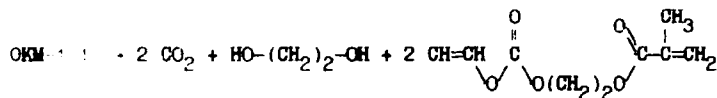
It was considered that OKM-1/1 scission takes place via intermolecular mechanism by carbonate and carboxylate groups (Schemes I and II).

Intermolecular scission of OKM, resulting via six-member transition state, leads to formation of CO₂, ethyleneglycole methacrylate (m.m. = 130) and unsaturated compound with m.m. = 200.

Intermolecular disintegration of OKM-1/0 (Scheme II) results in formation of methacrylic acid and vinyl derivative of OKM.

The comparison of Gibbs energy [Figure 6, (see 1 and 2)] shows that the scission





SCHEME IV

of carbonate group is thermodynamically more advantageous than that of carboxylate group.

In the case of polymer OKM-1/1 scission we assumed the Scheme III including one or two breaks of carbonate group.

The decrease of critical temperatures ($\Delta G_{p(cr.)}^T = 0$) (Figure 6) for OKM scission depends on the number of carbonate groups reacting by intermolecular mechanism.

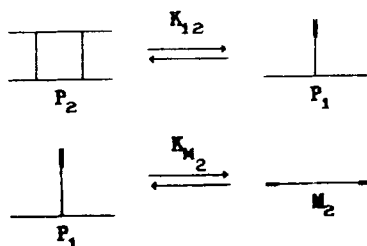
The thermodynamic stability of OKM homologous series does not depend on the molecular mass of OKM.

The degradation of OKM-1/1 (Scheme IV) by two carbonate groups through ethylene glycole formation differs insignificantly from the reaction (Scheme I).

The reactions of OKM scission by ester groups with polyanhydride fragments formation are thermodynamically more advantageous than the scission of carbonate groups. The critical temperature of this reaction is approximately 700°K (Figure 6).

5. DEPOLYMERIZATION THERMODYNAMICS OF NETWORK POLYMETHACRYLATES

The depolymerization scheme for polydimethacrylate networks based on bifunctional unsaturated ester is considered to consist of two equilibrium reactions: the reaction between the network polymer and its branched analogue and the reaction between the branched polymer and initial OEA (monomer)²⁰:



where P_2 and P_1 are the mole fractions of OEA reacted by two or one unsaturated group respectively, and M_2 represents the mole fraction of bifunctional OEA.

Every equilibrium reaction is characterized by its own equilibrium constant and its own values of heat and entropy of polymerization:

$$K_{12} = P_2/P_1 = 1/2 \exp \left(-\frac{\Delta H_{12} - T\Delta S_{12}}{RT} \right)$$

$$K_{M_2} = P_1/M_2 = 2 \exp \left(-\frac{\Delta H_m - T\Delta S_m}{RT} \right)$$

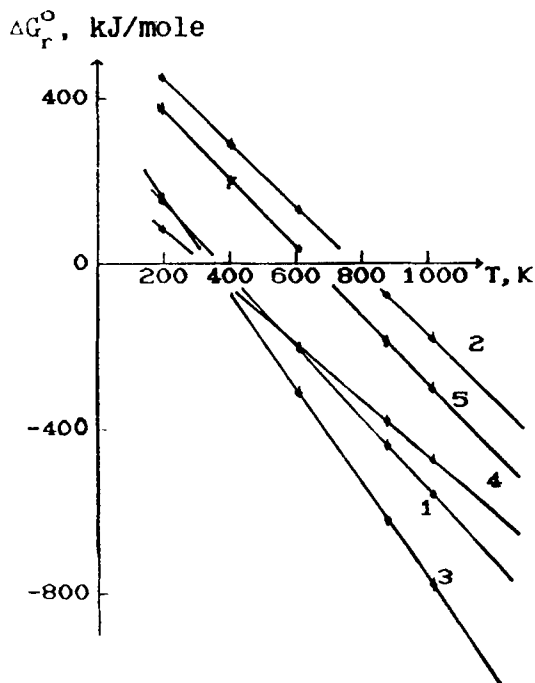
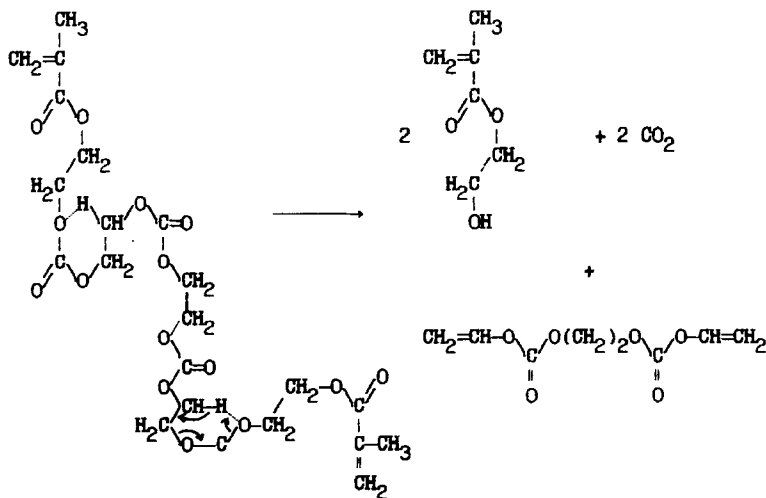


FIGURE 6 Dependence of Gibbs energy of reactions on temperatures: 1—intermolecular scission of OKM-1/0 by the Scheme I, 2—intermolecular scission of OKM-1/0 by the Scheme II, 3—scission of OKM-1/1 by the Scheme III, 4—scission of OKM-1/1 by the Scheme IV, 5—scission of OKM with formation of polyanhydro-fragments.



SCHEME III

The equilibrium concentration of monomer, M_2 , can be determined by means of its thermodynamical parameters

$$M_2 = \frac{\exp[(\Delta H_m - T\Delta S_m)/RT]}{2\{1 + 1/2 \exp[(\Delta H_{12} - T\Delta S_{12})/RT]\}} \quad (1)$$

If we take term β :

$$\beta = \exp[(\Delta H_m - T\Delta S_m)/RT] / \exp[(\Delta H_{12} - T\Delta S_{12})/RT]$$

and make some temperature assumptions, the Equation (1) can be simplified to Equations (2) and (4):

When $\exp[(\Delta H_{12} - T\Delta S_{12})/RT] \ll 1$,

$$M_2 = \exp[(\Delta H_m + \Delta H_{12} - T\Delta S_m - T\Delta S_{12})/RT] \quad (2)$$

or in logarithmic form

$$\ln[M_2] = \frac{\Delta H_m + \Delta H_{12}}{RT} - \frac{\Delta S_m + \Delta S_{12}}{R} \quad (3)$$

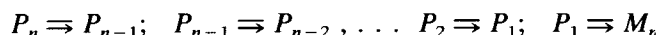
At high temperatures, when $\exp[(\Delta H_{12} - T\Delta S_{12})/RT] \gg 1$,

$$M_2 = 1/2 \exp[(\Delta H_{12} - T\Delta S_{12})/RT] \quad (4)$$

or

$$\ln[M_2] = \ln \frac{1}{2} + \frac{\Delta H_m}{RT} - \frac{\Delta S_m}{R} \quad (5)$$

The scheme of polyfunctional polymethacrylates depolymerization can be represented by



where P_i is the mole fraction of polyfunctional methacrylates reacted with i groups.

The analytical determination for M_n is

$$M_n = \frac{\exp[(\Delta H_m - T\Delta S_m)/RT]}{n \left(1 + \alpha'_2 + \alpha'_3 \alpha'_2 + \dots + \prod_{i=2}^n \alpha'_i \right)},$$

where $\alpha'_2 = \exp[-(\Delta H'_{12} - T\Delta S'_{12})/RT]$; $\alpha'_3 = \exp[-(\Delta H'_{23} - T\Delta S'_{23})/RT]$ etc.

Using the above Equations (3 and 5) and experimental data for equilibrium

TABLE III

The thermodynamic parameters of dimethacrylate esters polymerization

OEA	$-\Delta H_{(m)p}^{\circ}$ kJ/mole	$-\Delta S_{(m)p}^{\circ}$ J/mole*deg	$-\Delta H_{(12)p}^{\circ}$ kJ/mole	$-\Delta S_{(12)p}^{\circ}$ J/mole*deg	$-\Delta H_v$ kJ/mole	$-\Delta S_v$ J/mole*deg
ME	98, 5±3 (g - s)	224, 8±8 (g - s)	52, 5±3	95±8	42, 6	82, 7
	55, 3±3 (l - s)	141±8 (l - s)				
TGM -3	103±3 (g - s)	242±7 (g - s)	53±6	103±12	48, 9	91, 1
	54±3 (l - s)	151±7 (l - s)				

$-\Delta H_v$ and $-\Delta S_v$ are the heat and entropy of vaporization of monomers, respectively; g, l, s = gaseous, liquid and solid state. The values of heat vaporization were determined by Wall equation suggested for linear alkanes²⁸:

$$\Delta H_v = 13.42N^{2/3} - 0.0807T + 12.21, \text{ kJ/mole}$$

where N is the number carbon atoms in molecule.

Entropies of vaporization were estimated as $\Delta S_v = \Delta H_v/T_v$, where T_v is the temperature of vaporization.

concentrations (partial pressures) for dimethacrylate the thermodynamic parameters of polymerization reaction for network polymethacrylates were obtained.²⁰

To validate these relationships the PMMA ($M_n = 145000$) depolymerization \rightleftharpoons polymerization reaction was investigated in the temperature interval between 200–240°C. Using partial pressures values of monomers ME and TGM-3, we can obtain the thermodynamic parameters of polymerization reaction for gaseous monomer \rightleftharpoons solid polymer transition (Table III).²⁰

The obtained results allow us to compare the thermal stability of network and linear OEA polymers.²⁰

These data indicate that the thermal stability of network OEA polymers ($T_{cr.} = \Delta H_{(12)}^{\circ}/\Delta S_{(12)}^{\circ}$) decreases with increases of molecular mass and structure complexity of OEA. This trend is due to an increase in polymerization entropy while polymerization heat remains practically unchanged.

6. DEPOLYMERIZATION KINETICS OF NETWORK POLYDIMETHACRYLATES

The study of network MDPH polymers under low temperature pyrolysis (240–290°C) have shown that the initiation of chain depolymerization involves the break of “weak” or structure-stressed C—C bonds of the main polymer chains.¹⁸

The origin of stressed C—C bonds in OEA polymers depends on polymerization

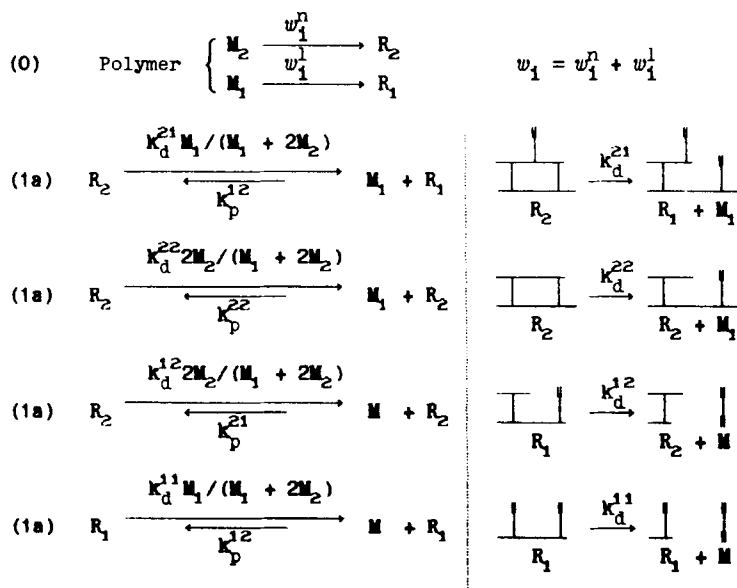
condition as well as heterogeneity of OEA structure. The thermal processing of OEA polymers (10–15°C above the temperature of molecular dynamics α -transitions) results in partial stress relaxation and increases of thermal stability. The analysis of products of mechanical and thermal degradation of MDPH polymer confirms the underlying relationship of these processes. It shows that thermal fluctuations play a main role in the thermal degradation of solid phase polymers.

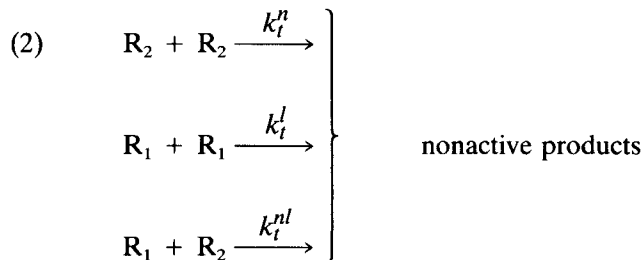
Two types of radicals (1 and 2) were registered in network polymethacrylates of ESR method, originating in the break of C—C bonds of the polymer main chains.^{17,18}



Linear PMMA forms only one radical type (1) in contrast to network polydimethacrylates. ESR double signal of type (3) radicals was registered at very severe thermal degradation.¹⁸ These radicals appear as secondary reactions of 1 and 2 type radicals. At 270–290°K the type 3 radicals transform into radicals 1.¹⁸ Therefore, the net polymethacrylates depolymerization is established as the chain radical process.

The ordinary kinetic depolymerization model for OEA polymers, in the absence of chain transformation is considered to consist of random scission initiation, depolymerization and termination reaction. This model takes into account the molecular heterogeneity of polymer structure and random distribution of linear fragments in polymer network.²³





M, M_1, M_2 —are the mole fractions of free monomer (OEA) and monomers reacted by one or two unsaturated groups respectively; R_2, R_1 —are network and linear polymer radicals; w_i —is the rate of depolymerization initiation; k_d —are the rate constants of depropagation for linear and network polymer radicals; k_p —are the rate constants of propagation (polymerization) for linear and net polymer radicals; $k_t^n; k_t^l; k_t^{nl}$ —are the rate constants of second-order and first order termination for polymer radicals R_1 and R_2 ; $M_1/(M_1 + 2M_2)$ and $2M_2/(M_1 + 2M_2)$ —are the probabilities of formation polymer radicals R_1 or R_2 during depropagation; $M + M_1 + M_2 = 1$.

We also assume that the constants of propagation (reverse of depropagation constants) are small in comparison with the rate constants of depropagation. In addition, the transformation of macroradicals depends on the first order termination for polymer radicals R_1 and R_2 because the depolymerization chains are sufficiently long.

From the above depolymerization model, the following rates correlations for formation M, M_1 and M_2 can be formulated.

$$\frac{dM_1/dt}{dM/dt} = \left\{ \frac{(\kappa_d^{22}/\kappa_d^{21}) + 1}{(\kappa_d^{11}/\kappa_d^{12}) + 1} \right\} \frac{2M_2}{M_1} - 1 \tag{6}$$

$$\frac{dM_1/dt}{dM_2/dt} = \left\{ \frac{(\kappa_d^{11}/\kappa_d^{12}) + 1}{(\kappa_d^{22}/\kappa_d^{21}) + 1} \right\} \frac{2M_2}{M_1} - 1 \tag{7}$$

$$\frac{dM_2/dt}{dM/dt} = \left\{ \frac{(\kappa_d^{22}/\kappa_d^{21}) + 1}{(\kappa_d^{11}/\kappa_d^{12}) + 1} \right\} \frac{2M_2}{M_1} - 1 \tag{8}$$

The assumption of a steady state radical concentration allows us to express the monomer rate formation.

$$\frac{dM}{dt} = (k_d^{11} + k_d^{12})k_d^{21}M_1 \frac{w_i^{1/2}(M_1 + M_2)}{[(k_t^n)^{1/2}k_d^{12}2M_2 + (k_t^l)^{1/2}k_d^{21}M_1] \rho}$$

where ρ is the polymer density to express the mole concentration.

The study of unsaturation degree for polymers ME and TGM-3 during the ther-

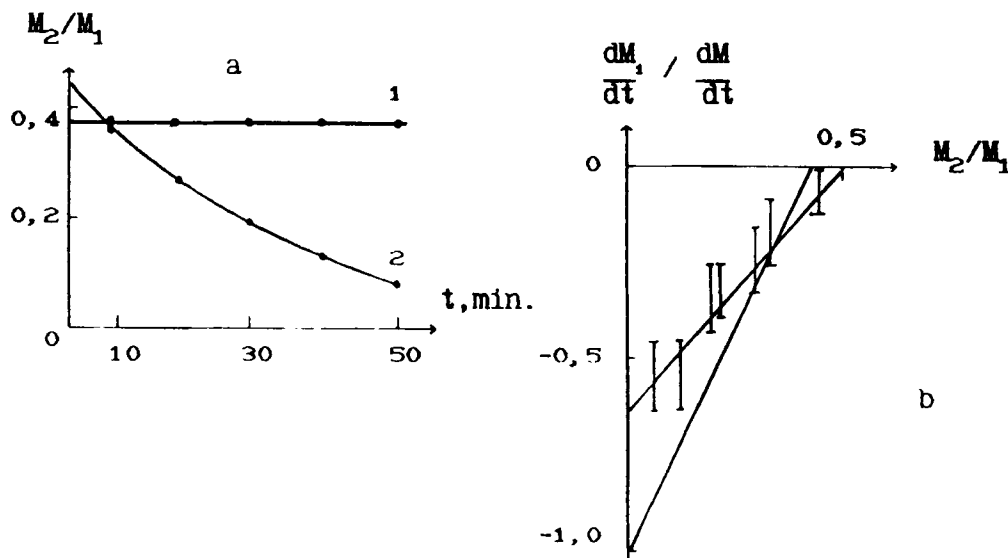


FIGURE 7 a—Dependence of unsaturation degree (M_2/M_1) of net polymethacrylates on time (t) during the depolymerization of PME (1) and PTGM-3 (2); b—Dependence of $(dM_1/dt)/(dM/dt)$ on M_2/M_1 during the depolymerization of PTGM-3 at 240°C.

mal depolymerization by IR and UV spectroscopy showed the constancy of value M_2/M_1 (ME) and decrease in this value for TGM-3 (Figure 7a).²³ From the relationship between $(dM_1/dt)/(dM/dt)$ and M_2/M_1 the correlation between the different rate constants of depropagation can be graphically determined (Figure 7). For the ME depolymerization (260°C) (Figure 7a) this correlation yielded $(\kappa_d^{22}/\kappa_d^{21} + 1)/(\kappa_d^{11}/\kappa_d^{12} + 1) = 2.65 \pm 0.20$. The computer iteration gives us the relative values for ME rate constants of depropagation.

$$\kappa_d^{11} = 0.727, \kappa_d^{12} = 1.309, \kappa_d^{21} = 0.441, \kappa_d^{22} = 1.377$$

In the case of TGM-3 depolymerization (240°C) the rate constants of depropagation correlation was determined from the slope of straight line, obtained from experimental results (with ordinate $[(dM_1/dt)/(dM/dt)] = -1.0$ and abscissa $(M_2/M_1) = 0$) (Figure 7b, line 1)

$$(\kappa_d^{22}/\kappa_d^{21} + 1)/(\kappa_d^{11}/\kappa_d^{12} + 1) = 1.25 \pm 0.08$$

However, a better agreement between the plotted points and experimental results is graphically indicated by line 2 (Figure 7b).

This fact can be explained assuming an increase of formation rate for monomer in real process as compared with the suggested kinetic model. The increase of monomer formation rate can be attributed to: 1) The fact that the rate constants of propagation (reverse of depropagation constants), k_p^{ij} , are comparable to the rate constants of depropagation, κ_d^{ij} . 2) Existence of isolated structure cycles in TGM-3 polymer which can directly form the initial monomer.

The theoretical model as well as experimental values of effective activation energies of OEA polymers thermal degradation allow us to estimate the kinetic parameters of elementary depolymerization reactions for network OEA polymers. Experimentally determined effective activation energies (E_{eff}) for thermal degradation of ME and TGM-3 polymer networks under isothermal heating at the conversion ($1 - w/w_0$) of 0.1–0.15 are equal to 82.8 and 79.4 kJ/mole respectively. At high levels of conversion these E_{eff} increase to 144.2 and 169.3 kJ/mole.²³

The higher values of E_{eff} reflect a change towards the initiation involving the law of probability, namely the random scission of C—C bonds.

The effective activation energies for depropagation of linear polymer fragments (E'_d) of ME and TGM-3 are equal to 118.3 and 123.7 kJ/mole respectively. For the network fragments the values of E''_d are equal to 73.5 kJ/mole (ME) and 74 kJ/mole (TGM-3).²³

The values of the effective activation energies for termination of linear polymer radicals (E'_t) are equal to 163.2 kJ/mole (ME) and 160.9 kJ/mole for TGM-3. The values of the effective activation energies of initiation according to random scission of C—C bonds are equal to 215.0 (ME) and 276.0 kJ/mole (TGM-3).²³

Thus, the assumed model allows us to estimate the kinetic parameters of formation of the network fragments and randomly distributed linear fragments of polydimethacrylates. Note, however, that this model is the first kinetic approximation for cross-linked polymethacrylates depolymerization. Further quantitative studies will be required to take into consideration the mathematical models of random distribution for microheterogeneous globular structures in network polymer matrix as well as the models for the self-organized type of cross-linked polymethacrylate structure.

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