

CCA-834

YU ISSN 0011—1643

547.49

Original Scientific Paper

Thermo-oxidative Stability and Flammability of Three-dimensional Polymers Based on Olygocarbonate-methacrylates

P. M. Aseeva, A. A. Berlin, B. A. Ushkov, B. T. Shashkova, and
T. Ya. Kefeli

The Institute of Chemical Physics, Academy of Sciences of the USSR,
Moscow, USSR

Received June 15, 1974

By the irreversible condensation reaction of the mono-methacrylic ester of ethylene glycol and chlorocarbonic esters of 2,2-dimethylpropanediol-1,3 and 2,2-dimethylene chloride-propanediol-1,3, two olygocarbonate methacrylate (OCM-I and -II, respectively) containing unsaturated ends were synthesised. The polymerization of OCM-I and OCM-II in the presence of cumene hydroperoxide and an accelerator gave two cross-linked polymers in a yield of 70—75%.

The thermal and thermo-oxidative decompositions of the prepared polymers were studied by the thermogravimetric method and by characterization of the volatile pyrolysis products and the nonvolatile polymer residue. The influence of the polymer structure on the mechanism of the decomposition reactions *in vacuo* as well as in the presence of oxygen was discussed. The temperature dependence of thermostability was compared with some polymer flammability parameters.

The olygocarbonate-methacrylates (OCM) represent a relatively new class of olygoesters with regular structure which contains the end unsaturated groups of acrylic type and carbonate groups in a molecular chain¹.

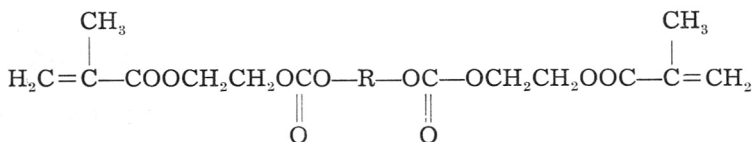
OCM are interesting in the production of organic glasses, construction and electro-insulating materials, sealants *etc.*, due to their good dielectric and optical properties, their favorable physico-mechanical characteristics and heat resistance.

It is necessary to note that there are no data in literature about the kinetics and mechanism of thermal and thermo-oxidative decomposition of this class polymers and of their flammability. Naturally, the flammability of polymers is of special interest. However, there is a tendency now to a more interconnective study of kinetics and mechanism of slow chain reactions during the polymer pyrolysis and oxidation, and of the high temperature reactions during their burning.

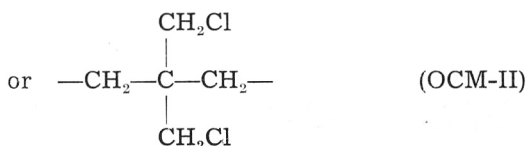
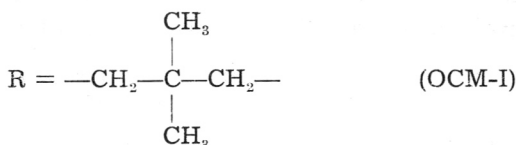
Apparently this is connected with the fact that polymer burning in the presence of oxygen (close to diffusion flame) is characterized² by an independent polymer pyrolysis zone and the flame zone.

The regularities of thermal and thermo-oxidative decomposition of two polymers based on OCM have been investigated.

OCM have the following general formula:



where



The results of the investigation of the thermostability and the decomposition products were compared with some parameters characterizing the polymer flammability.

EXPERIMENTAL

Olygocarbonate—methacrylates I and II were obtained by the low temperature irreversible polycondensation of the chlorocarbonic esters of 2,2-dimethyl-propanediol-1,3 and of 2,2-dimethylene chlor¹de-propanediol-1,3 with the monomethacrylic ester of ethyleneglycol in methylene chloride in presence of pyridine (HCl acceptor).

The physical and chemical properties of the synthesized OCM are given in Table I. The OCM polymerisation were accomplished at room temperature in the presence of 0.5% cumol hydroperoxide and 0.1% accelerator B. The samples for the decomposition study were pounded on a vibromill and seeded; the fractions with the grain size of 100—150 mesh were selected. Then, in order to remove the non-reacting OCM, the samples were extracted by acetone in a Soxhlet apparatus and heated in vacuum (10^{-4} atm) at 70—80 °C for 3.5 hours. The degree of polymerisation as defined by i.r. spectroscopy was 70—75%.

TABLE I
Physico-chemical properties of olygocarbonate-methacrylates

Specimen	Acid number mg KOH/g	Bromine value g Br/100 g		Molecular weight		n_D^{20}	d_n^{20}	η_{sp}	Elemental composition* %		
		found	calcd	found	calcd.				C	H	Cl
OCM-I	0.0	76.2	76.84	410	416.4	1.4642	1.660	352	54.35	6.68	—
									54.80	6.78	—
OCM-II	0.2	64.95	65.92	480	485.4	1.4842	1.2780	3500	47.42	5.37	14.42
									47.01	5.40	14.63

* Upper figures — found, lower figures — calculated.

The polymer destruction kinetics was studied by the weight method; for this purpose the automatic balances ATB-2 and ATB-200 were used and, also, the derivatograph of F. Paulick, I. Paulick and Erdei. The substance weight was 20–60 mg.

Al_2O_3 served as the standard in determining the thermal effects; the calibration was accomplished according to $\text{K}_2\text{Cr}_2\text{O}_7$. The volatile products of polymer destruction were analyzed by means of the mass-spectrometer MX-1303 and by the method of rising thin-layer chromatography on alumina.

The system of eluents was as follows: benzene—acetone (95:5% by volume), developer—water solution (0.3%) of KMnO_4 and $\text{K}_2\text{S}_2\text{O}_8$.

The oxygen index and self-ignition point temperature were determined by ASTM 2863 and by the method described in ref. 3. The linear velocity of sample ($100 \times 6 \times 2$ mm) burning was determined at the oxygen content in a mixture with nitrogen being 27% and in atmosphere adequate to that of polymer oxygen index.

RESULTS AND DISCUSSION

The thermogravimetric curves of given polymers are shown in Fig. 1; they were obtained in vacuum (10^{-4} atm) with the constant rate of temperature rising being 3 K/min. It is clear that the intensive polymer decomposition under vacuum begins at the temperatures higher than 250 °C. Two steps can be distinguished on the curves, reflecting apparently the change of the character of the pyrolytic process.

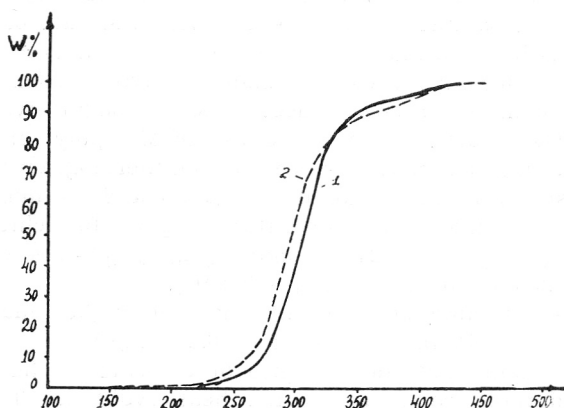


Fig. 1. TG curves of three-dimensional polymers based on OCM-I (1) and OCM-II (2) *in vacuo* (10^{-4} mm Hg) at a heating rate of 3 K/min.

It is interesting to note that the introduction of voluminous electron-acceptor substituents (chlorine atoms) into the OCM molecule reduces the temperature at which an intensive evolution of volatile products begins.

At the constant heating rate up to 300–320 °C or at the isothermal exposure to vacuum at (225 ± 1) °C for 2.5 hours the volatile products of the pyrolysis of three-dimensional polymer were found to be colourless matters, condensating at room temperature.

The pyrolysis products consist of (as determined by thin-layer chromatography) the original OCM ($R_{f,OCM-I} = 0.47$; $R_{f,OCM-II} = 0.48$); a small quantity of dimers ($R_{f,dOCM-I} = 0.31$) and OCM trimers ($R_{f,tOCM-I} = 0.06$) is caused apparently by the secondary polymerization of generated oligomers.

Heating under more severe conditions (330 °C) causes the formation of CO₂, water, CH₂O, vinyl- and ethyl-methacrylates, dimethyl (the OCM-I polymer) or dimethylene-chloride derivatives of ethylene (the OCM-II polymer) to take place as well as the volatilization of OCM.

In this way the rupture of carbon-carbon linkages of the main chain and depolymerization have occurred during the three-dimensional OCM pyrolysis in vacuum at moderate temperatures (up to 300–320 °C) as well as in the case of oligoester-methacrylate MDF-2 polymer⁴. By increasing the temperature the depolymerization of space-reticular OCM polymers was observed, as well as the rupture of bridge blocks linkages.

Apparently due to limited mobility of OCM three-dimensional net fragments the decomposition of carbonate bridge bonds has not corresponded entirely to the Ritchie scheme for the asymmetrical aliphatic carbonates pyrolysis⁵. This decomposition is complicated by the formaldehyde chipping and by the formation of unsaturated hydrocarbon or chlorohydrocarbon combinations. The combinations containing the hydroxyl groups (*e.g.* alcohol and glycol) were not found in the volatile products of OCM pyrolysis. These groups are typical for carbonate decomposition according to β -chipping by Ritchie. This can be connected with the methodic factors. It should be noted that the HCl evolution during the OCM-II pyrolysis has not been observed.

Oxygen intensifies and complicates the polymer destruction process. The derivatograms of the samples, heated in air with the rate of 4.2 K/min are shown in Fig. 2. As it was already observed in vacuum, the chlorine-containing polymer begins to decompose earlier than its hydrocarbon analogue. The temperature at which an intensive decomposition begins was easily determined from the DTG curve to be 217 °C for OCM-I polymer and 187 °C for the chlorine-containing polymer. However, on the thermogram the temperature at which the first exothermal peak begins (T_{exo}) and its maximum position (T_{max}) are moved to the high-temperature region for chlorine-containing OCM-II polymer ($T_{\text{exo,OCM-II}} = 271$ °C and $T_{\text{max,OCM-II}} = 294$ °C as compared with $T_{\text{exo,OCM-I}} = 233$ °C and $T_{\text{max,OCM-I}} = 278$ °C).

The chlorine-containing polymer also has the higher maximum rate of volatiles (R_{max}). It is 1.44 mg/K instead of 0.813 mg/K for OCM-I polymer. It is interesting to note that the presence of chlorine in the OCM molecule leads to a considerable reduction of the heat evolution. The heat of the oxidative exothermal reaction determined by the area of the first exothermal peak is decreased from (-94.0 ± 10) cal/g to (-27.0 ± 10) cal/g for the chlorine-containing analogue. The calculation of derivatograms for the OCM-II polymer by the method of Reiche *et al.*⁶ shows that, up to 12% conversion, the thermo-oxidative destruction process is realized according to the first order reaction with the effective activation energy $E_{a,\text{eff}}$ = (38.5 ± 3) kcal/mol. The value of the pre-exponential factor is 3.2×10^{14} min⁻¹.

The TG curves for the OCM polymers, taken during the heating in air in isothermal conditions, are shown in Figs. 3 and 4. The curves have autocatalytic character which has no connection with the presence of variable-valent vanadium (the rest of the activator of OCM polymerization) in the polymer. The thermo-oxidative decomposition of the sample obtained by thermal polymerization of OCM-I was the same. The curves of such a form are typical for branched-chain-radical processes of oxidation of the organic substances.

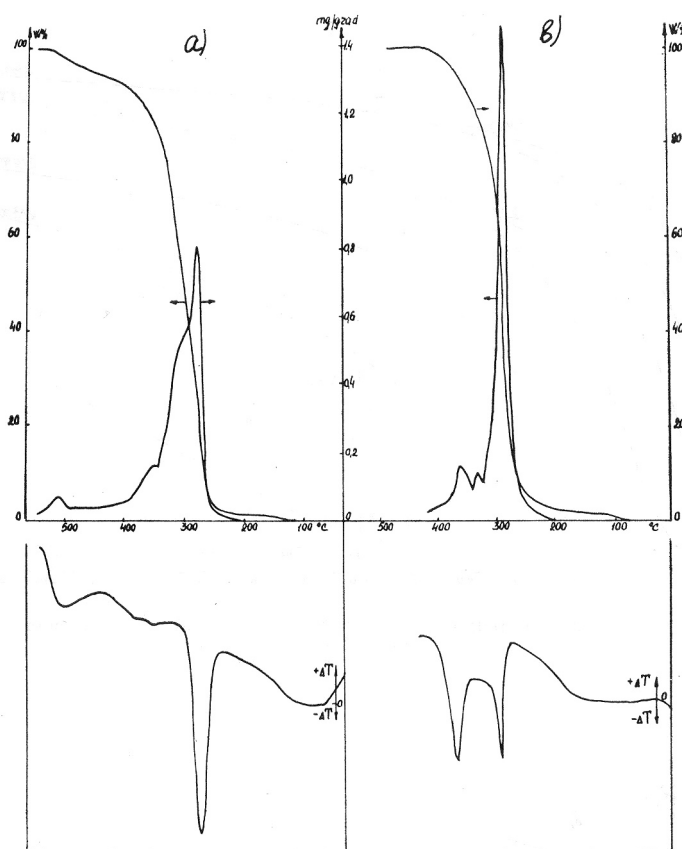


Fig. 2. The derivatograms of polymers based on OCM-I (a) and OCM-II (b) heated in air with a rate of 4.2 K/min.

Apparently the autocatalysis of the OCM polymers studied is caused by the rupture of ester linkages in carbonate groups and by the formation of chain reticulating products.

The analogous three-dimensional polymers on the base of oligoester-methacrylates are decomposed on air without acceleration. During the heating of the OCM-II polymer in air at the temperature of 216 or 228 °C for 4 hours volatile products containing no CO₂ are evolved with a constant rate (Fig. 4). The volatile pyrolysis products represent high-boiling combinations, condensing and polymerizing on the vessel walls during the outlet from the pyrolysis zone.

I. r. spectra of non-volatile polymer residue did not change except for the intensification of the band $\nu_{C=C} = 1640 \text{ cm}^{-1}$.

These results lead to the conclusions that oxygen attacking the methylene groups of macromolecule main chains, initiates the depolymerization of three-dimensional polymethacrylate. However, due to the high pressure, the OCM is evaporated slowly and can therefore undergo secondary reactions. At the

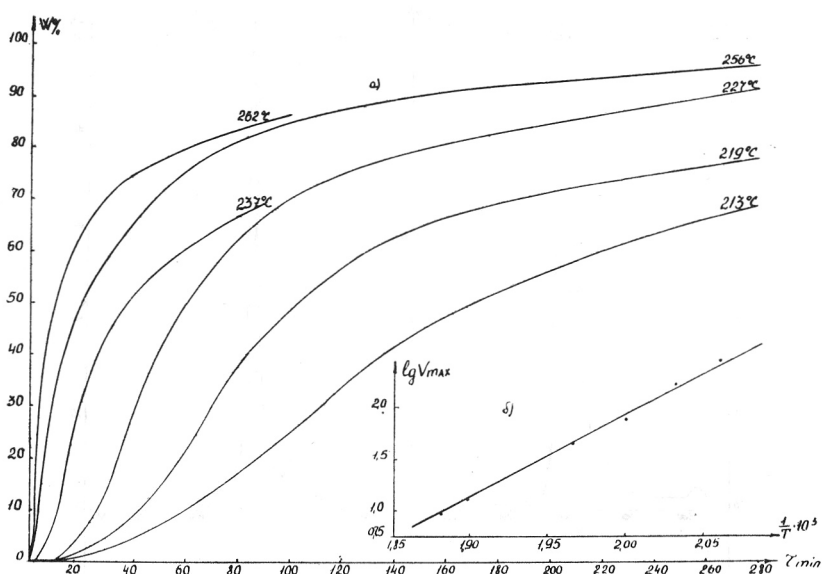


Fig. 3. TG curves of OCM-I polymer heated in air (a) and the dependence of $\lg V_{\max}$ on $1/T$ (b).

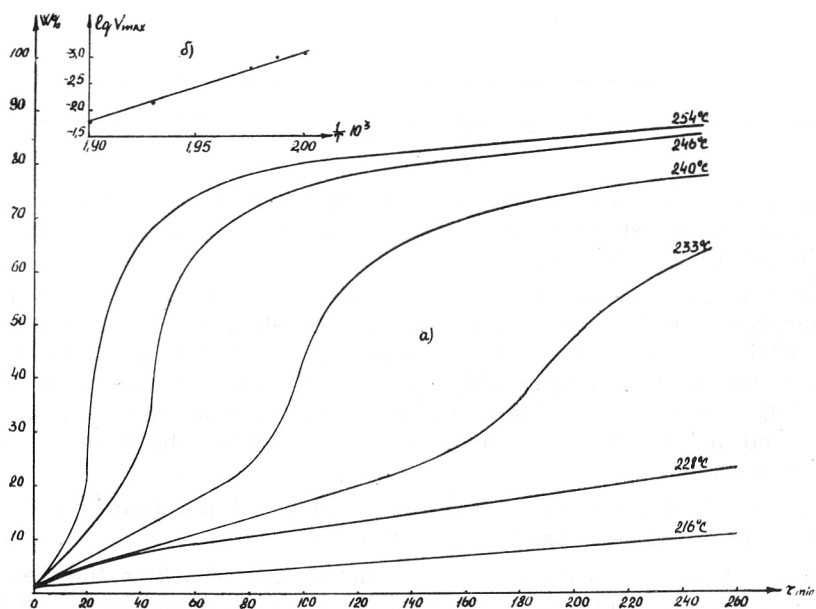


Fig. 4. TG curves of OCM-II polymer heated in air (a) and the dependence of $\lg V_{\max}$ on $1/T$ (b).

elevated temperatures ($> 233^{\circ}\text{C}$) the rupture of ester bonds and the evolution of CO_2 was observed.

The thermo-oxidative decomposition of chlorine-containing polymer was not accompanied by the formation of free HCl . It was impossible to separate (by thin-layer chromatography) the high-boiling volatile products of the polymer oxidation, which were condensing on the pyrolytic cell walls. However, the change in i. r. spectra of these products (the appearance and the subsequent increase in intensity of ν_{OH} at 3500 cm^{-1} the change of relative intensity of $\nu_{\text{C}=\text{O}}$ at 1715 , 1750 and 1780 cm^{-1} and $\nu_{\text{C}-\text{O}}$ at 1260 and 1160 cm^{-1}) points out the different rates of oxidative decomposition. It is interesting to note that thermo-oxidative destruction of the chlorine-containing OCM-II polymer in isothermic conditions proceeded slower than that of its hydrocarbon analogue.

Values of the calculated (by maximum velocity of volatile products eduction) effective activation energies were as follows: (36 ± 2) kcal/mol for OCM-I polymer and (56.5 ± 2) kcal/mol for OCM-II polymer (Fig. 3b, 4b).

The value of $E_{a,\text{eff}}$ for the thermo-oxidative destruction of three-dimensional OCM-II polymer obtained by means of isothermal curves, is significantly higher than that obtained by derivatogram [(38.5 ± 3) kcal/mol]. It is much higher than $E_{a,\text{eff}}$ found for an oxidation process of various organic compounds. This is an apparent contradiction: halogen introduction into the OCM hydrocarbon radical causes the polymer decomposition (the initial temperature of the evolution of volatiles is increased), but at the same time this introduction retards the velocity of the evolution of volatiles. Apparently, this fact is connected with the change of the elementary reactions of the decomposition process, *i. e.* the reactions of initiation and of chain termination.

The presence of voluminous polar chlorine atoms in the OCM molecule causes the appearance and concentrations of stress in the space-reticular polymer and, therefore, causes the weakening of some bonds and their rupture because of fluctuation at heating.

In other words structural factors are influenced on the initiation of the OCM polymer decomposition process. At the same time it is possible to suppose that chlorine — containing fragments of the reticular polymer or chlorine hydrocarbon products of its destruction take part in reactions kinetics of chain termination and decrease in this way the velocity of polymer decomposition. The higher decomposition rate of the chlorine-containing polymer, observed at its heating at air in dynamic conditions (Fig. 2) does not contradict what has been said before.

As the position of the TG peak of chlorine-containing polymer is moved to a higher temperature relative to its hydrocarbon analogue, and $E_{a,\text{eff}}$ is higher, the value of R_{max} for OCM-II is higher than that of OCM-I polymer.

It is interesting to note, that the regularities observed for the thermo-oxidative decomposition of the OCM polymers are correlated with some parameters characterizing their flammability. For example, the self-ignition temperature of the chlorine-containing polymer is 30°C lower than that of

its analogue. It is possible that this 30 °C difference in the temperatures for the beginning of the oxidative decomposition and in the temperatures of their self-ignition is a simple coincidence; but the general tendency is not fortuitous.

One of the main indices of polymer flammability is the so-called oxygen index (OI)². According to that, the studied polymers are flammable. But in comparison with a linear analogue — polymethylmethacrylate (OI of PMMA = 17.5²) the studied three-dimensional OCM polymers are relatively less flammable. This is partly caused by the ability of the polymer to decompose with the formation of CO₂.

The introduction of chlorine atoms into OCM molecule increased the polymer OI up to 19.3 and decreased the rate of specimen burning down to 0.061 mm/s (Table II).

TABLE II
Some indices of flammability of polymers based on OCM

Indices	Specimen	OCM-I polymer	OCM-II polymer
Oxygen index		18.5	19.3
The burning rate in atmosphere, corresponding to that of OI/mm s ⁻¹		0.067	0.061
The burning rate in atmosphere, containing of 27% of oxygen/mm s ⁻¹		0.310	0.390
The self-ignition point temperature/K		441	411

Apparently, the observed facts are connected with the inhibition of the burning process by the chlorine-containing products of polymer decomposition, similar to the inhibition of specimen thermo-oxidative decomposition at low temperatures.

It is usually believed that the stationary burning of specimens in an atmosphere whose composition had been adjusted adequately to OI takes place at the stoichiometric concentration between the fuel and the oxidant. In this case diffusion flames may be considered as the fuel-rich flames. In the work by Baratov *et al.*⁷ the influence of haloidhydrocarbon combinations on burning of fuel-rich and fuel-deficient mixtures is considered. The rate of polymer burning is increased with the increase of the oxygen content in the atmosphere. But the rate of chlorine-containing polymer burning is higher.

This fact is probably connected with an increase in the surface temperature of the burning polymer, occurring due to an increase of heat flow from flame to polymer; in the case of fuel-deficient flame it is not inhibited by chlorine-containing substances⁷.

REFERENCES

1. A. A. Berlin *et al.*, *The author licence USSR N 215497, 16.08.06, Bull. of inventions*, N 32, 1971, USSR.
2. P. L. Warren, *SPE Journal* **27** (1971) 17.
3. V. M. Monakhov, *The methods of fire dangerous studies*, Khimiya, Moscow 1972, p. 246.
4. P. M. Aseeva, *Vysokomol. soedin. Ser. A* **14** (1972) 1573.
5. P. D. Ritchie, *J. Chem. Soc.* (1935) 1054.
6. L. Reich, K. T. Lee, and D. W. Levi, *J. Polym. Sci.* (1963) 535.
7. A. H. Baratov and E. I. Ivanov, *The Fire Extinguishing in Chemical, Petrochemical and Petroleum Works*, Khimiya, Moscow 1971, p. 73.

SAŽETAK

Termo-oksidacijska stabilnost i upaljivost trodimenzionalnih polimera oligokarbonatnih estera metakrilne kiseline

P. M. Aseeva, A. A. Berlin, B. A. Ushkov, B. T. Shashkova i T. Ya. Kefeli

Opisana je priprava dva oligokarbonatna estera metakrilne kiseline kondenzacijom monoetilenglikol-metakrilata s esterom klorugljične kiseline i 2,2-dimetil-propandiola-1,3 odnosno 2,2-diklormetil-propandiola-1,3. Polimerizacijom nastalih monomera uz kumen-hidroperoksid dobiveni su trodimenzionalni polimeri s iskorištenjem od 70—75%. Ispitana je termička i termo-oksidacijska stabilnost polimera metodama termogravimetrijske analize i karakterizacijom produkata pirolitičke razgradnje. Prikazan je odnos nekih parametara upaljivosti polimera prema temperaturnoj ovisnosti količine i vrste razgradnih produkata.

INSTITUT ZA KEMIJSKU FIZIKU,
AKADEMIJA ZNANOSTI SSSR
MOSKVA, SSSR

Primljeno 15. lipnja 1974.