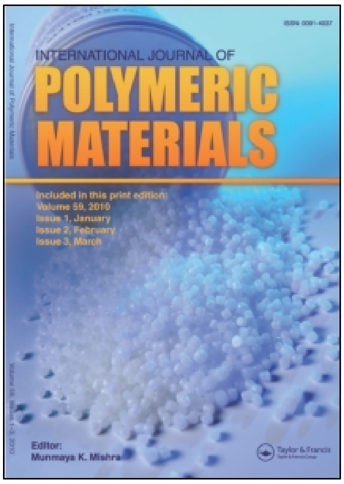

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Size-Exclusion Chromatography of Highly-active Organometallic and Multifunctional Metal-Containing Compounds

L. M. Antipin[a]
[a] Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia

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Size-Exclusion Chromatography of Highly-active Organometallic and Multifunctional Metal-Containing Compounds

L. M. ANTIPIN

Institute of Physical Chemistry, Russian Academy of Sciences,
Moscow 117071, Russia

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Some results of size-exclusion chromatography (SEC) investigations of highly-active organometallic and metal-containing highly-active compounds (OMC) are reviewed. Until recently these classes of compounds have not been investigated by chromatography. New labile multifunctional metal-containing oligomers is revealed. The further application of SEC investigation for MW-analysis of highly-active OMC and multifunctional elementoxide compounds are outlined. The basises of labile multifunctional hetero-organic oligomers chemistry are founded.

Keywords: Organometallic compounds; high activity; analysis; size-exclusion chromatography

INTRODUCTION

Some highly-active organometallic compounds (OMC) are unstable. These monomers and oligomers undergo quick changes and are readily hydrolyzed and oxidized. Until now adsorption liquid chromatography [1] (LC) has not been applied to high-active OMC, because these compounds react irreversibly with inorganic sorbents. It seems perspective to study the possibilities of size-exclusion chromatography (SEC) to determine molecular weight (MW) distributions of active OMC and multifunctional metal-containing compounds. LC analyses has not been applied to them and other methods of evaluation give little information and insufficient evidence. If correct evaluations of SEC data on OMC were possible, even their initial characterization would be essential.

This is the beginning of chemistry of high-active organometallic and metall-containing multifunctional labile oligomers and intermediates.

PECULIARITIES OF THE METHOD

The methods used are typical for handling spontaneously combustible OMC. All the operations were carried out in an inert atmosphere. The eluents were carefully dehydrated and kept in darkness and inert atmosphere with the solid metal hydrides and inert atmosphere.

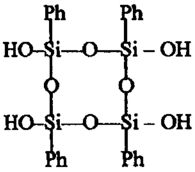
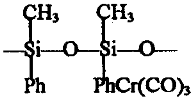
Before the analysis the chromatographic (C) columns were trained, for example, by the solutions of $[Me_3Si_2]NH$ for multifunctional organosiloxane compounds (OSC), $—Al(iC_4H_9)_3$, for organoaluminium compounds (OAC), $—TiCl_4$ for titanium chlorides.

To analyze the compounds with high reactive properties the training of the C column was carried out using the substances being analyzed until the accurate reproduction of the results is provided. The standards for these investigations are not available. These standards were synthesized (for example, by hydrolytic condensation of $Si(OC_2H_5))$ or selected experimentally from oligomers or monomers of the class of substances investigated, preparatively separated and characterized using independent methods. The data on some substances used for calibration are presented in Table I (column 100/0,9 cm, gel SDV-J, granules 0,2–0,5 mm, eluent-dried toluene, 2 ml/min, refractometer RIDK-101, CSFR). The ratios given in examined range of molecular weights (MW) the beginning of sizing scale-in semilogarithm coordinates lg MW – V_e is closed to linear [2].

RESULTS AND DISCUSSION

Aluminiumtrialkyls (AA) and their derivatives aluminiumalkylhalogenides, alkylaluminiumhydrides and other OAC are separated on the

TABLE I Experimental data and Moor's equation for different elementoxide oligomere

Initial monomer or		*Experimental*		*Moore's equation*
oligomer link	*MM*	*lgM*	*V_e, ml*	*V_e =*
	1122	3,05	30	$V_e = 173,4-47,0\,lgM$
	1740	3,24	20	
	720	2,857	39,5	$V_e = 175,5-47,6\,lgM$
	1360	3,133	26,5	
	1470	3,167	24,5	
	1660	3,220	23,0	
$TiCl_4$	190	2,279	58,0	$V_e = 139,99-35,99\,lgM$
	249	2,397	53,0	
	317	2,501	50,0	
$Ti(OC_4H_9)_4$	340	2,532	41,7	$V_e = 101,25-23,8\,lgM$
	550	2,740	35,6	
	760	2,881	31,0	
	1630	3,2124	24,5	
$Al(C_2H_5)_3$	114(theor)	2,057	34,0	$V_e = 53,52-9,52\,lgM$
	186(theor)	2,268	32,0	
$Al(iC_4H_9)_3$	198	2,299	28,0	$V_e = 50,94-9,84\,lgM$
	298	2,475	26,0	
	638	2,806	23,0	

SEC columns by the sieve mechanism. SEC of the samples of industrial AA show (Fig. 1) the presence of some OAC with the different MW. To increase the separation efficiency of magnesium-aluminum alkyls supercross-linked gel stirosorb [3] was used. In toluene solutions of compounds investigated transformations of the type.

$Mg_nAl_mR_{2n+3m} \rightleftarrows MgR_2 + AlR_3$, and other association-dissociation reactions take place (Fig. 2). SEC of Mg-AA shows, that their nature is more complex, than it might have been expected on the basis of the data of cryoscopy and other methods of investigation. Grignard reagents (Gr) leave the column forming a peak (with positive Gilman test), which in its upper part is tripled, forming a crown (Fig. 3). It have been observed formerly that Gr after treatment by dioxan-1,4

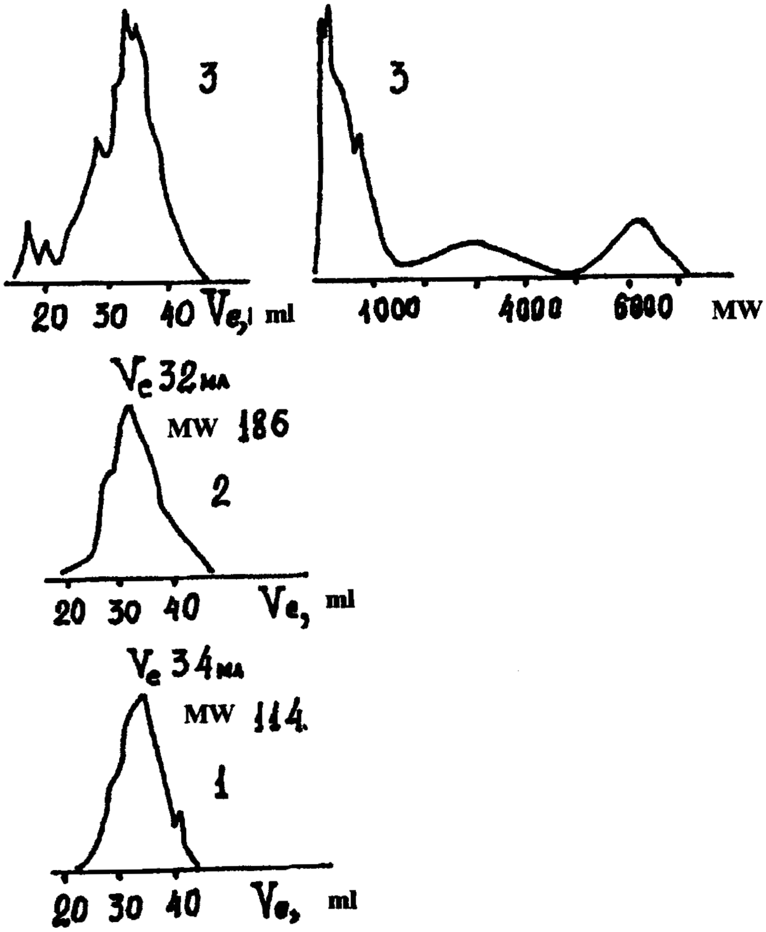


FIGURE 1 Chromatograms and molecular weight distribution (MWD) for the sample of industrial aluminiumtriethil and ethylalumoxanes. 1-triethylaluminium, 2-tetraethylalumoxane, 3-products of triethylaluminium hydrolise.

have been symmetriced [4]:

$$2C_4H_9MgCl \bullet 2(C_2H_5)_2O \xrightarrow{\text{dioxan-1,4}} (C_4H_9)_2Mg \bullet \text{dioxan-1,4} + MgCl_2 \bullet O(C_2H_5)_2 \rightarrow (MgCl_2)_x.$$

The SEC data are in conformity with the generally accepted opinion [4]. Ti and Al-containing high-molecular substances are formed upon

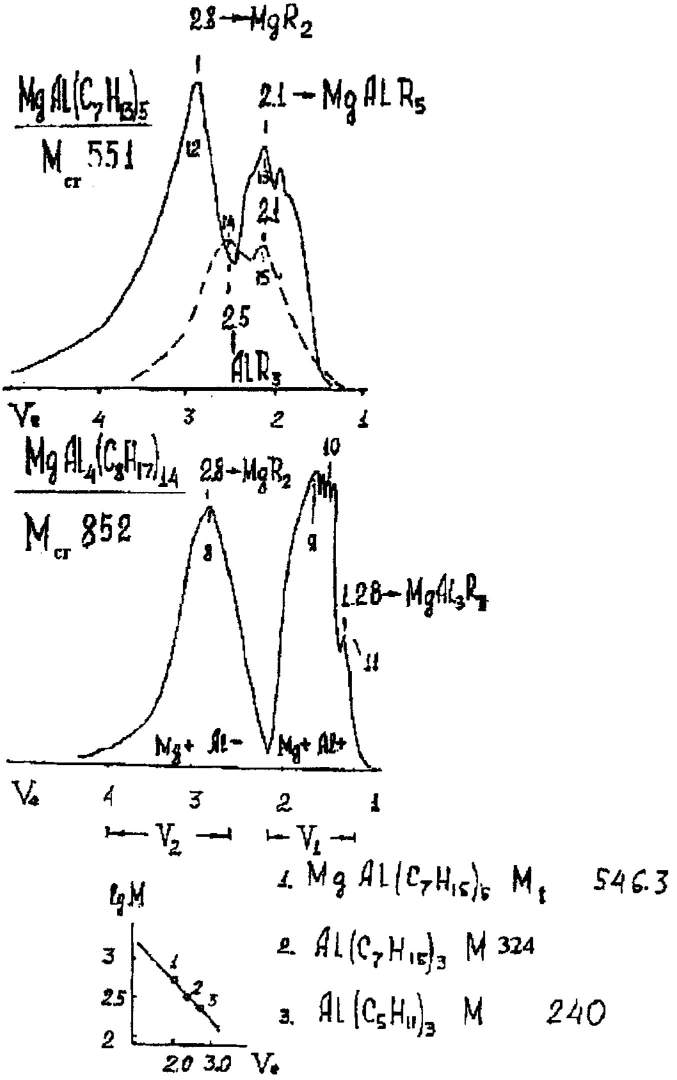


FIGURE 2 Chromatograms and calibration curve with standards used for magnesium-aluminium alkyles, gel–stirosorb, column 260/4 mm, toluene, 2 ml/min; V_1 and V_2-volumes of samples yielded.

homogenous interaction of $(acac)_2$ $TiCl_2$ and (C_2H_5) AlCl (Fig. 4). These high-molecular catalysts are responsible for formation of polypropen. These catalysts may be characterized by the growth of

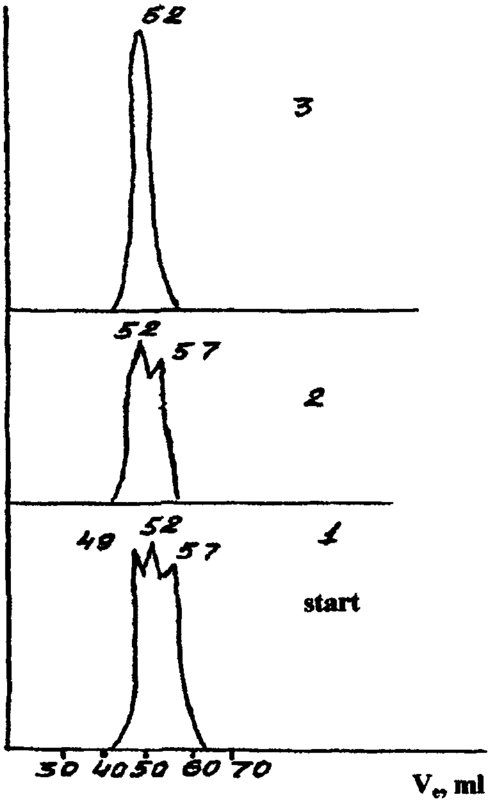


FIGURE 3 The products of $C_4H_9MgCl \bullet 2(C_2H_5)_2O$ transformation by dioxan-1,4: 1-initial, 2-a loss of dioxan 3-an excess of dioxan.

their own MW followed by the loss of their solubility, precipitation and loss of catalytic properties. The deposition of these homogenous catalysts (nuclei of clusters) on the surface of polymer gel substrates [5] excludes polycondensation, that leads to the decay of active catalytic centres. The stability of catalytic systems deposited on polymer gels as well as the stability of their action [5] at temperatures to 200°C increase. The description of the direct methods of determination of high-molecular components in technical $TiCl_4$ are not available. The use of SEC allows their preliminary estimation to be made. In the cubic residue after a single distillation of technical $TiCl_4$ (Fig. 5) there are both high-and lowmolecular substances (Tab. II). The V_e 49–50 ml

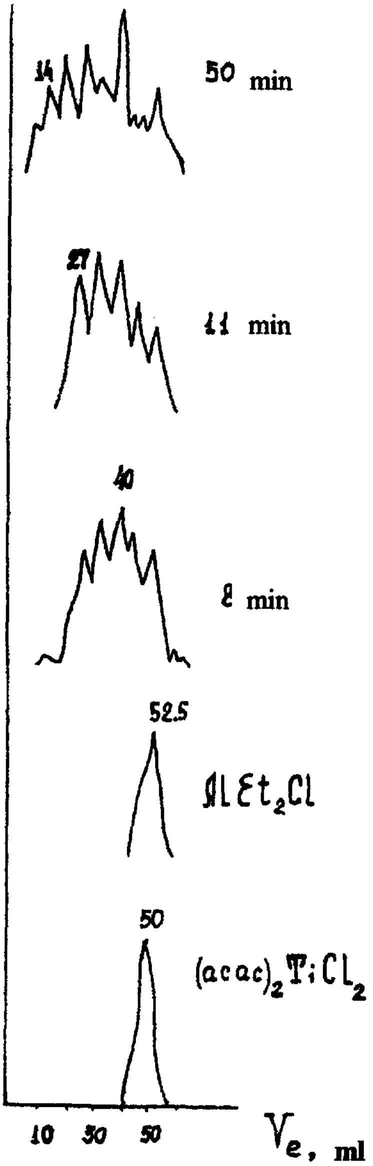


FIGURE 4 Chromatograms of dissolved Ziegler catalytic complex and start components.

fraction in all the samples are dyed. The possibility of preparative insolation of the oligomer components is the precondition for the calibration correction of the further elucidation MW. The differential curve of the MW distribution for homogenous hydrolysate of $Ti(OC_4H_9)_4$ show the presence of a substance (Fig. 6), similar to $Ti(OH)_4$ by its MW [6].

The interaction of $SnCl_4$ with excess $Ti(OC_4H_9)_4$ gives resinous noncrystallizing product. This product readily decomposes upon distilla-

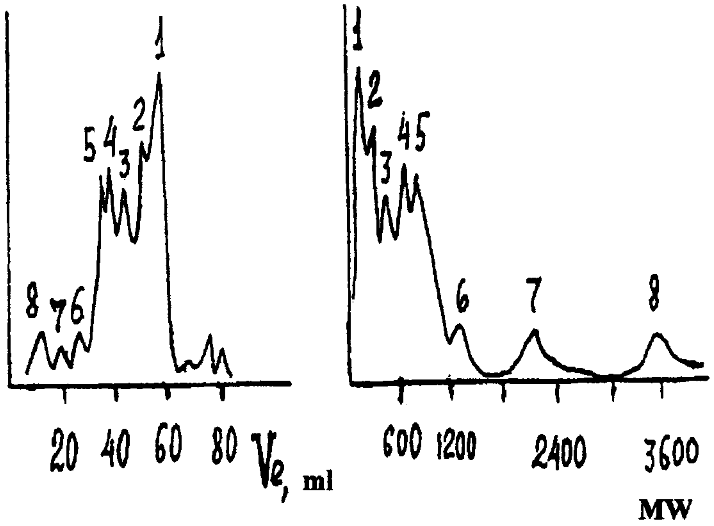


FIGURE 5 Chromatograms and differential MWD curve for the sample of cubic residue after a single distillation of technical $TiCl_4$.

TABLE II Compounds, present in cubic residue after a single distillation and in the partial hydrolyzed sample $TiCl_4$

V_e, *ml*	M_{sec}	M_{theor}	*Probable formula*
64,5	126	116	$Ti(OH)_4$
58,0	190	190	$TiCl_4$
50,0	317	325	$Cl_3Ti\text{-}OTiCl_3$
44,0	464	460	$Cl_3Ti(OTiCl_2)_2Cl$
37,5	706	730	$Cl_3Ti(OTiCl_2)_4Cl$
35	830	865	$Cl_3Ti(OTiCl_2)_5Cl$
28,0	1299	1270	$Cl_3Ti(OTiCl_2)_8Cl$
20	2162	2215	$Cl_3Ti(OTiCl_2)_{15}Cl$
12	3620	3565	$Cl_3Ti(OTiCl_2)_{25}Cl$

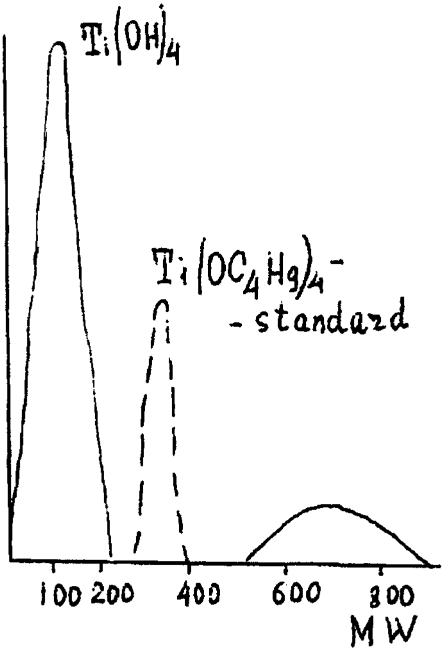


FIGURE 6 The MWD curve of tetrabutyltitanate homogeneous hydrolise products.

tion; its main fraction, according to SEC-data, has 1260 dalton (Fig. 7). During this interaction C_4H_9Cl is distilled off in near to equimolecular quantities. The liquid product has catalytic activity during liquid-phase oxidation of *n* $C_{15}H_{32}$ by oxygen to acid, equal to that of Co-stearate. MW for $Sn[OTi(OC_4H_9)_3]_4$ is 1250 [7]. Individual $Ti(OR)_4$, $SnCl_4$ or their mixtures have not any catalytic properties. It may be assumed that the origin of the catalytic activity observed results from formation of the Sn-O-Ti fragment. Other alkoxides of two oxygen-bonded elements (for example Al-O-Ti, Al-O-Si, Ti-O-P *etc.*) have been obtained analogically and estimated in terms of the MW distribution. The use of SEC allows one to control the interaction of components and to stop it at a necessary moment.

SEC-investigation of products of hydrolyses $Si(OC_2H_5)_4$ allows one to define more precisely the concepts about chemism of this process, to establish the destruction hydrolytic instability of siloxane oligomers under normal conditions [8]. Silazane oligomers are unstable too.

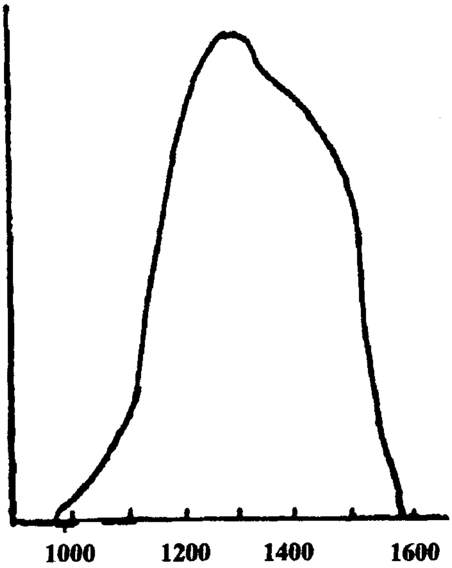


FIGURE 7 The MWD curve of interaction $SnCl_4$ with $Ti(OC_4H_9)_4$ excess products.

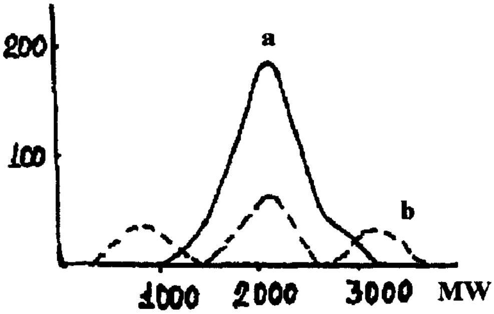


FIGURE 8 The MWD curves of olygomersilazane MSN-7: a-initial, b-after 10 h contact with moisture of air.

Upon contacting oligomer silazanes with air moisture (in the case of oligomer metylsilazane MSN-7, Fig. 8) there is not only MW decrease, but also observed increase. This circumstance is connected, probably, with the condensation of silanols formed in the process of hydrolis Si-N groups. Amins group catalyses the condensation of silanols.

There are oligoacetoalumoxane (MW ~410 – 470) in the thermolysis products of $Al(OCOCH_3)_3$ water solution (Fig. 9). These compounds were unknown early. Column 270/11 mm, sephadex LH-20, H_2O 2 ml/min, volume of sample 1%(weight) – 0,5 ml. The sizing scale is linear on the base of aluminum salts water solutions.

New data, obtained by means of SEC-investigations OMC, represent new, earlier unavailable information about MW state of these compounds. This new information cannot give answers to all the unsolved questions and gives rise a lot of new ones. Nevertheless

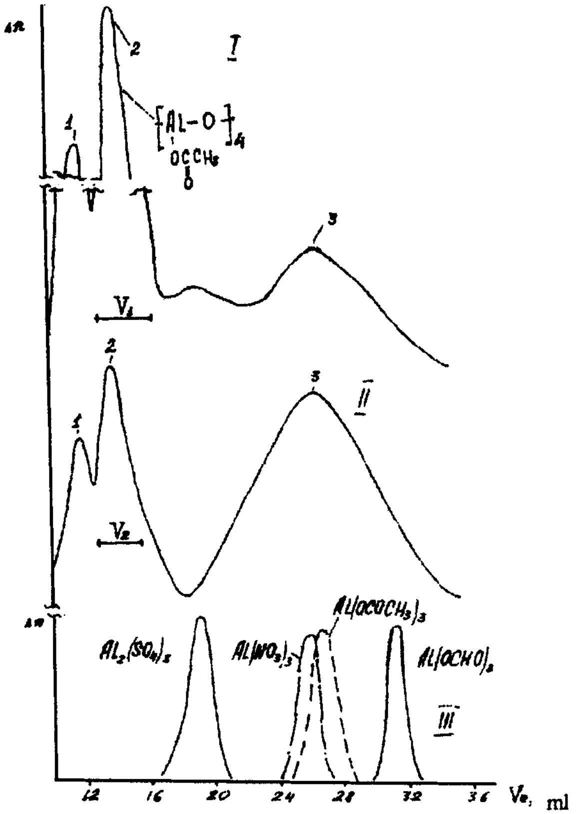


FIGURE 9 Termolysis products of $Al(OCOCH_3)_3$ water solution (I-5 h, 210°C; II-8 h, 190°C), III-standards for sizing scale. V_1 and V_2-preparatively separated samples, containing Al and acetate groups. Probable structures of alumoxane oligomers are shown.

informationable of SEC-investigations of highactive OMC and analogous compounds is clear from the mention examples.

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