Complexing of Organoaluminum Compounds with Polyethers and Polyacetals

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ABSTRACT

This work is concerned with the study of the complexing reaction between the low molecular weight V-acceptor, diethylaluminum chloride (DC), and polymeric donors containing oxygen, such as poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), polytetrahydrofuran (PTHF), polyformaldehyde (PF), poly(phenylene oxide) (PPO), polydioxolan (PDO), and polytrioxocan (PTO). Three types of complexes, 1:1, 2:1, and 1:2, were detected in solution. In the case of PEO, the thermodynamical parameters of the 1:1 complex formation are $\Delta H_1 = -23.3 \pm 0.5$ kcal/mole, $K_1 = (5 \pm 2) \times 10^5$ liter/mole, $\Delta S_1 = -51.5 \pm 2.4$ eu, while those of the 1:2 complex formation (0.2A1) from the 1:1 adduct are $\Delta H_{III} = -18.5 \pm 0.6$ kcal/mole, $K_{III} = 0.9 \pm 0.3$ liter/mole, $\Delta S_{III} = -62.3 \pm 2.9$ eu. Two structures were found in the case of 1:1 polymer-acceptor complexes.

EXPERIMENTAL

Since diethylaluminum chloride (DC) and its complexes are rather sensitive to oxygen and moisture, all experiments were carried out with their exclusion (dried solvents, argon atmospheres) [1].

The purified DC had the following characteristics: $d_{20}^{20} = 1.0059$, bp = 125-126°C/50 Torr. The polymers were purified on ion exchange resins with subsequent drying on vacuum column in a thin layer. The polymer molecular weight ranged from 3000 to 44000.

The IR spectra of the starting components and their complexes were obtained on a UR-10 spectrophotometer in the region of 3200-2600 and 2000-400 cm^{-1} in hermetically sealed cuvettes (layer thickness 17-25 μm) with salt (KBr and NaCl) and germanium windows. The cuvettes were filled in a dry box in a flow of dry argon.

Thermochemical data were obtained on a Calve calorimeter. The calorimeter constants were: heat input constant, 9.625×10^{-7} cal/mm-sec, heat take-off constant 1.673×10^{-4} cal/mm, time constant $\tau = 166$ sec.

The NMR spectra were taken on a high-resolution Varian HA-100 instrument (at 100 MHz) at 29°C. Toluene was used as internal standard; the reference peak was that of toluene at 7.17 ppm with respect to TMS (0 ppm).

The molecular weight distribution of the polymer samples was determined on a Waters chromatograph. The porous materials were polystyrene Waters gels with characteristics 10^5- 10^6 Å; the solvent was tetrahydrofuran; 25°C; the polymer concentration was 0.3-0.5 wt %.

RESULTS AND DISCUSSION

The thermodynamical parameters were computed from heat evolution versus initial component concentrations. The system of diethylaluminum chloride and poly(ethylene oxide) was investigated by this method [2]. When PEO was titrated with DC acceptor the amount of heat evolved per DC (deficiency) constituted 23.3 ± 0.5 kcal/mole. There is a change in slope of the plot of heat evolution at a 1:1 ratio (Fig. 1). However heat evolution continued upon further addition of the acceptor, which could be a result of addition of another DC molecule to the oxygen.

We found also (Fig. 2) that the amount of heat increases at a considerable excess of the polymeric donor (the number of monomeric units exceeds six times the number of Et_2AlCl) even at the low
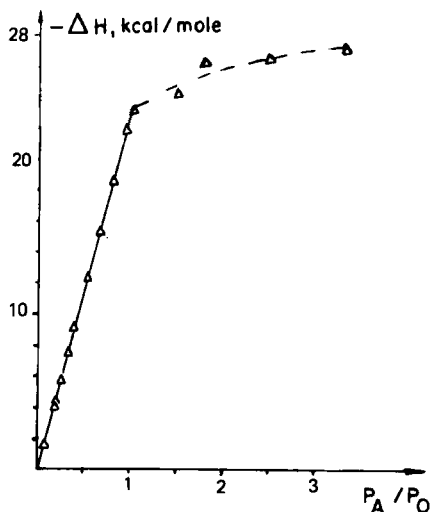
FIG. 1. Plot of heat evolution vs. Al:0 ratio.

concentration of the polymer (below 0.04 mole/liter). This demonstrates the formation of pentacoordinated aluminum producing two donor-acceptor bonds with the oxygens of the same polymeric chain. Thus we observed three types of complexes in solution: 1:1, 2:1, and 1:2 complexes.
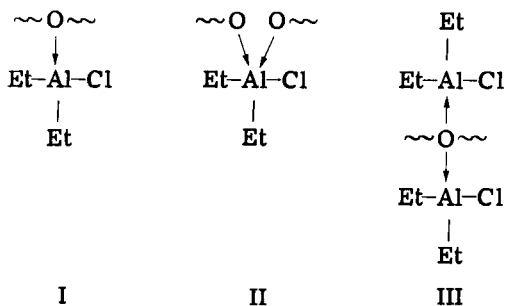
The formation of complex I may be depicted by the scheme (1).

$$2 \,-OCH_2 \, CH_2 - \, + \, Et_4 \, Al_2 \, Cl_2 \xrightleftharpoons{K_I} 2 \,-OCH_2CH_2$$

$$Et_2 AlCl \qquad (1)$$

FIG. 2.   Plot of heat evolution vs. donor concentration (at an acceptor deficiency).

The relation for the constant K_1 obtained by solving the system of four independent material and heat balance equations has the form:

$$K_I = 2/[\, C_A (1 - \eta)(\eta\alpha - 1)^2 \,]$$

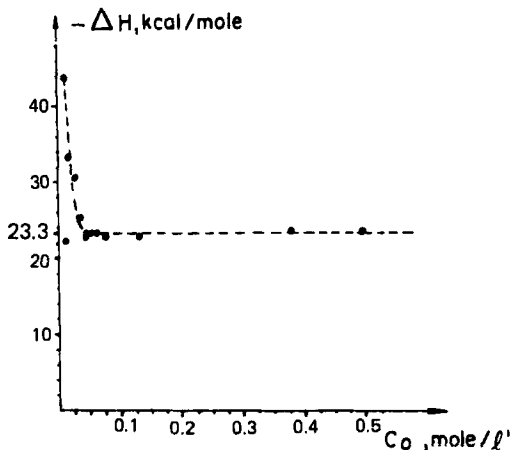where $\eta = (q/nA)/\Delta H_I$ is the degree of conversion, q is the heat evolved in a calorimeter, C_A and n_A are the initial concentration and the amount of acceptor (moles), respectively, α is the ratio of initial concentrations of the monomer units of polymer and acceptor.

The thermodynamic parameters of formation of complex I are listed in Table 1.

If the principal difficulties in determining K_1 are due to an essential reaction shift toward the formation of complex I then the formation of adduct II cannot be described quantitatively, due to considerable intermolecular interaction. In such a case one may cite only the magnitude of the heat of formation of complex II greater or equal to -44.0 ± 0.5 kcal/mole, i.e., the maximum value obtained experimentally.

The formation of tetracoordinated oxygen may be given by Eq. (2).

TABLE 1. Thermodynamic Parameters of Formation of Different Types of PEO and DC Complexes at 25°C

Process	K (liter/mole)	$-\Delta H$ (kcal/mole)	$-\Delta S$ (eu)
Formation of complex I	$(5 \pm 2) \, 10^5$	23.3 ± 0.5	51.5 ± 2.4
Transition from I to II	-	≥ 20.7	-
Transition from I to III	0.9 ± 0.3	18.5 ± 0.6	63.3 ± 2.9

$$2 \, Et_2AlCl \leftarrow \overset{\iota}{\underset{\iota}{O}} + Et_4Al_2Cl_2 \underset{}{\overset{K_{III}}{\rightleftharpoons}} 2 \, Et_2AlCl \leftarrow \overset{\iota}{\underset{\iota}{O}} \rightarrow Et_2 \, AlCl \qquad (2)$$
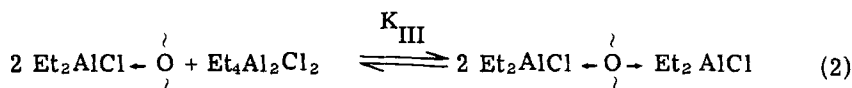
The expression for K_{III} has the form:

$$K_{III} = 2 / \left\{ \left[C_A - (1 + \beta) C_0 \right] \left[(1/\beta) - 1 \right]^2 \right\}$$

where the degree of complex I to III transformation β is given by

$$\beta = (\Delta H_0 - \Delta H_1) / \Delta H III$$

We note that the results obtained for process III are valid at low donor concentrations (up to 0.2 mole/liter). At the higher concentrations an intermolecular interaction of the chains is quite essential and no formation of complex III was observed.

The presence of 1:1, 2:1, and 1:2 complexes in solution was confirmed by investigating the polytetrahydrofuran-DC system.

The reaction of DC with other polymeric donors was also studied [3]. The 1:1 adducts formation enthalpies are listed in Table 2.

As can be seen from Table 2, the donor activity of the polymeric donors is approximately the same but exceeds those of the low molecular weight ligands (diethyl and dibutyl ethers). PPO is an exception. The essentially lower heat in such a case may be due to the p-π conjugation of the free electron pair of the oxygen with the π-electronic system of phenylene radicals. The energy of pπ-conjugation in PPO is close to 6.4 kcal/mole.

In addition to investigation in solution, the complexes were subjected to the IR spectral study in the solid state [4].

TABLE 2. Heats of DC 1:1 Complex Formation with Various Donors (25°C, Toluene)

Donor		$-\Delta H \pm 0.5_1 (kcal/mole)$[a]
PEO	$-CH_2-CH_2-O-$	23.3
PTHF	$-CH_2-CH_2-CH_2-CH_2-O-$	25.0
PTO	$-CH_2-O-(-CH_2CH_2-O)_2-$	23.4
PPO	$-O-C_6H_4-$	17.4
$(C_2H_5)_2O$		22.2
$(C_4H_9)_2O$		22.2
PDO	$-CH_2-O-CH_2-CH_2-O-$	23.7

[a]The heats are given for the reaction:

$$0.5\ Et_4Al_2(sol) +\ \sim O\sim(sol) = Et_2AlCl \longleftarrow \overset{\wr}{\underset{\wr}{O}}\ (sol)$$
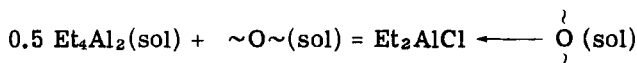
Reasons were found to explain the differences in the IR spectra of complexes from simple summing up the spectra of initial compounds. They involve: the change of electronic density at the atoms producing the donor-acceptor bond, a change in symmetry of the molecules entering the reaction, and distortion of the crystalline structure of the polymer.

Figure 3 shows the IR spectra of initial components (DC, PEO) and their complexes of different chemical composition. The spectra are arranged according to increasing acceptor content in the samples: spectrum 3 refers to the complex with generally 3.22 monomer units per monomeric acceptor molecule. The chemical composition of the polymeric samples maximally saturated with acceptor was 1:1. No 2:1 and 1:2 complexes were found in the solid phase, which is in good agreement with thermochemical data in solution.

At the same time there is proof for the existence of two different structures (IV and V) of 1:1 complex in condensed phase. These two structures of the same chemical compositon show different IR spectral characteristics.

The specificities of "macrodonors" associated with their polymeric character include conformational transformations in the course of complex formation. The change in the infrared absorption of PEO
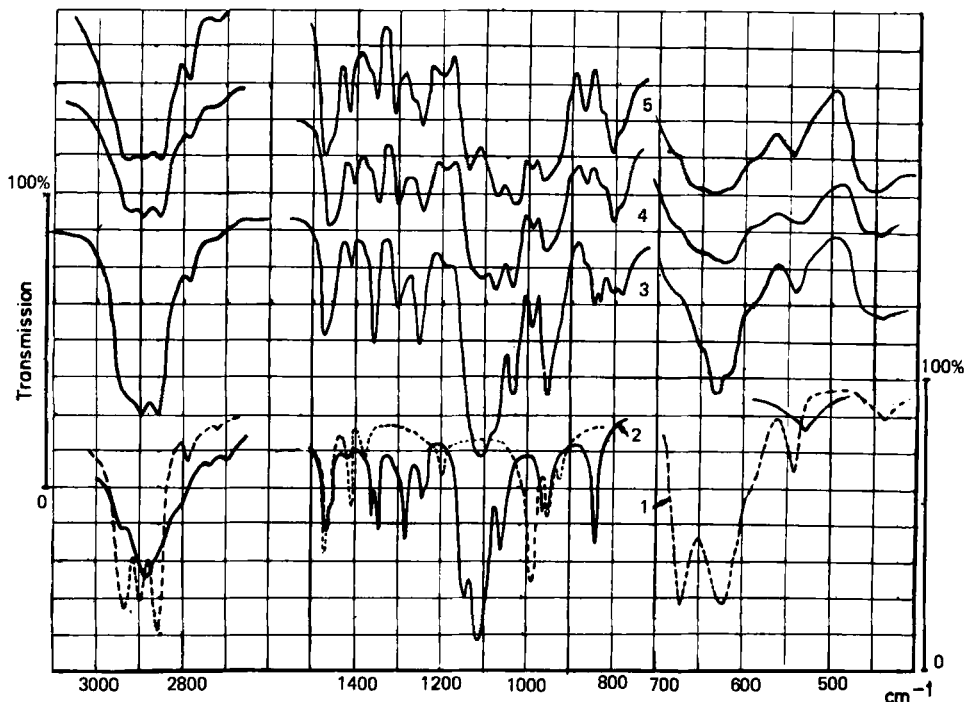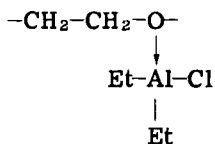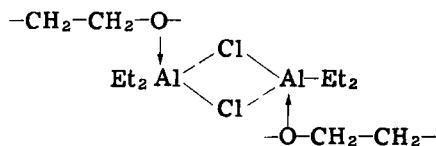
FIG. 3. IR spectra of (1) $Et_4Al_2Cl_2$, (2) poly(ethylene oxide), and (3-5) their complexes.

$-CH_2-CH_2-O-$
$\downarrow$
$Et-Al-Cl$
$|$
Et

IV

$-CH_2-CH_2-O-$
$\downarrow$
Et_2Al $\diagdown$ Cl $\diagdown$ $Al-Et_2$
         Cl $\uparrow$
                    $-O-CH_2-CH_2-$

V

due to the variation of macrochain conformation in complexing was observed as well. The 7_2 spiral (TGT form) specific to free PEO macromolecules is transformed entirely into a planar zigzag (TTT-form). This is evident from disappearance of bands at 1360 and 849 cm^{-1} which, in terms of literature data, are assigned to the TGT
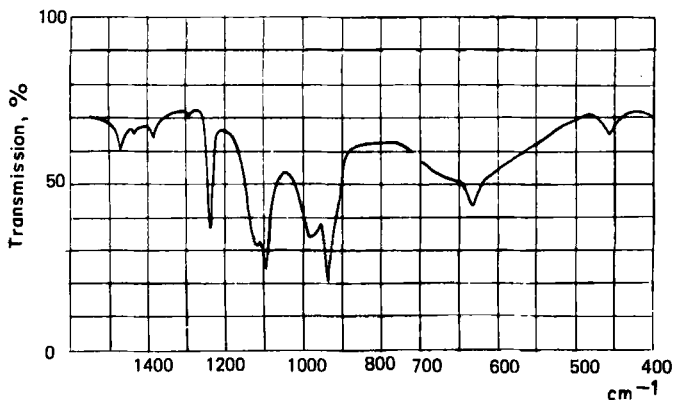
FIG. 4. IR spectra of polyformaldehyde in TT conformation.

conformation of PEO, and from the appearance of absorptions at 1348 and 869 cm^{-1} (TTT form).

The IR spectra demonstrated the change of polyformaldehyde conformation on complexing with DC: the GG form (spiral 9_5) is transformed completely into the TT conformation (planar zigzag) (Fig. 4).

According to the literature data, PP molecules in the TT form display such absorption. This permits one to clarify the dependence of IR spectral absorption of PP on its conformation since the methods existing (preparation of the melt, lyophilic drying) lead only to some partial change in the structure of PP macromolecules. Thus the band at 1239 cm^{-1} which is rather intense in the IR spectrum (Fig. 4) in our opinion is independent of rotational isometry of the macro-chain.

Polyacetals differ essentially from polyethers in their reaction with DC in that the chain-breaking reaction proceeds via the complexation step.

The reaction products of polyacetals of PDO and PTO with DC were investigated by use of NMR and IR spectral methods. Along with co-ordination compounds we have revealed the presence of degradation products of the type R—OAl(Cl)Et (where R denotes the polymer chain fragment) generated in the reaction shown in Eq. (3).

$$R\text{--O--R} \longrightarrow R\text{--O--Al--Et} + Et\text{--R} \qquad (3)$$
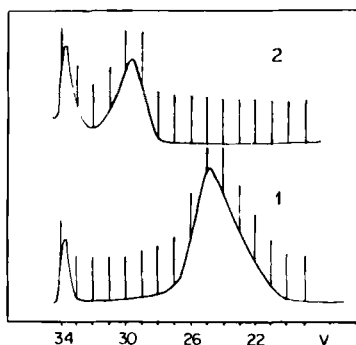$$\underset{Et_2Al\text{--Cl}}{\big|} \qquad\qquad \underset{Cl}{\big|}$$
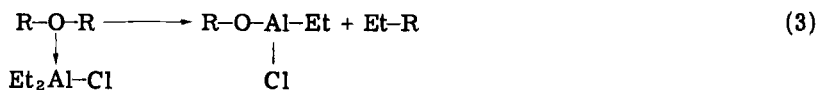
FIG. 5. Chromatography of PPO: (1) initial; (2) regenerated from the complex.

The change of molecular weight distribution MWD and molecular weight MW of polyacetals were investigated by gel-permeation chromatography and viscometry. Figure 5 shows the gel chromatogram of the initial PDO sample and that generated from the complex. An increase in the elution volume V_p showing the maximum yield of regenerated PDO from the chromatograph demonstrates the low molecular weight shift of MWD.

Since in the presence of DC the polyethers do not undergo degradation, the cleavage of polyacetals is explained by the presence of the acetyl O—C—O bond. It was found also that not all acetyl bond cleave. Even in the presence of an excess of acceptor the molecular weight of a macromolecule decreases to a certain value, after which the cleavage reaction is completed. For example, the molecular of PP sample decreased from 3980 to 525 after treatment with an acceptor.

CONCLUSIONS

The existence of three types of complexes with DC (1:1, 2:1, and 1:2) was demonstrated by using PEO and PTHF. Possible structures for these complexes are proposed.

The heats of formation of 1:1 complexes in the polymeracceptor system were determined.

The possibility for determination of the p-π conjugation in the

heteroatom-containing polymers was demonstrated. Thus in poly-(phenylene oxide), the energy of p-π conjugation is equal to -6.5 $\pm$ 0.5 kcal/mole.

In the condensed phase, 1:1 polymer-acceptor complexes of two structures displaying different spectral characteristics were demonstrated.

Formation of complexes was found to involve conformational changes in the macrochain. Thus poly(ethylene glycol), when saturated with an acceptor is transformed completely from the spiral 7_2 (TGT form) into the planar zigzag (TTT form); polyformaldehyde also changes its 9_5 spiral conformation into the TT form.

The presence of $-O-C-O-$ acetal bond was shown to be responsible for cleavage of polyacetal complexes.

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