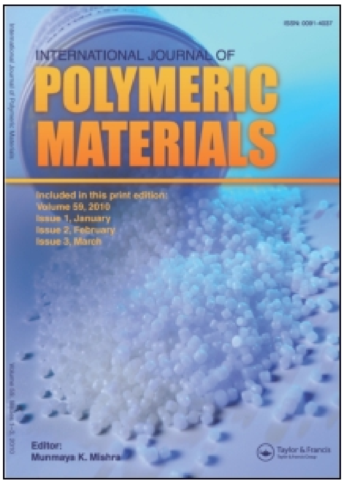

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Besruckov, A. , Deryabina, O. , Maharinsky, L. , Halturinsky, N. and Berlin, A.(1990) 'Pyrolysis of Model Sulfur-Containing Compounds in Molten Salt $NaAlCl_4$', International Journal of Polymeric Materials, 14: 1, 101 — 107

To link to this Article: DOI: 10.1080/00914039008041076

URL: http://dx.doi.org/10.1080/00914039008041076

Intern. J. Polymeric Mater., 1990, Vol. 14, pp. 101–107
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Printed in the United Kingdom

Pyrolysis of Model Sulfur-Containing Compounds in Molten Salt $NaAlCl_4$

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The authors experimentally investigated pyrolysis of model vulcanized butadiene compounds with different sulphur content on the melt of $NaAlCl_4$. The maximum yield of liquid pyrolysis products occurs at 400°C, and is independent on S content. There was also observed strong desulphurization of liquid products, due to removal of S with the pyrolysis gases in the form of H_2S. On the basis of same experiments on desulphurization of model mixture $C_{16}H_{34}S$ with $C_{15}H_{32}$ with the same catalyst was proposed possible mechanism of S removal through the formation of stable complexes.

KEYWORDS: Pyrolysis, sulphur-containing compounds, polymer waste utilization, rubber, yield, products

Recently many researchers have investigated different ways of polymer waste utilization. The main problem in this field is, of course, the reclamation of rubber waste. In the USSR it is mainly used tyres (about 1.7 mln tonnes per year). At present only about 25% of used tyres are utilized. All the existing known commercially available methods of rubber utilization have their technological drawbacks. Among the most promising methods is the pyrolysis of rubber in the stream of inert gas and in molten salts. According to the existing publications in this field, some salts do not have catalytic properties and act only as heat-conducting media. Melts, containing strong Lewis acids, such as $AlCl_3$, have strong catalytic properties.

This work is devoted to the experimental investigation of pyrolysis of some model compounds, containing sulfur, in the media of $NaAlCl_4$. This salt according to Refs 1–2 is a good catalyst of destruction, and also has good thermal properties—high conductivity, low temperature of crystallization (150°C).

The catalyst was obtained by melting of equimolar amounts of NaCl and $AlCl_3$ under the Ar atmosphere. The experiments were conducted in the apparatus. The scheme is given in Figure 1. The apparatus consists of quartz vessel, with total volume about 300 cm^3, equipped with a thermocouple well, a neck for sample introduction. Steady flow of dry Ar of about 0.3 cm^3 per second was blown through the apparatus. The gases passed through the water-cooled condenser then the Drecksel traps filled with the 5% water solution of Cd acetate to

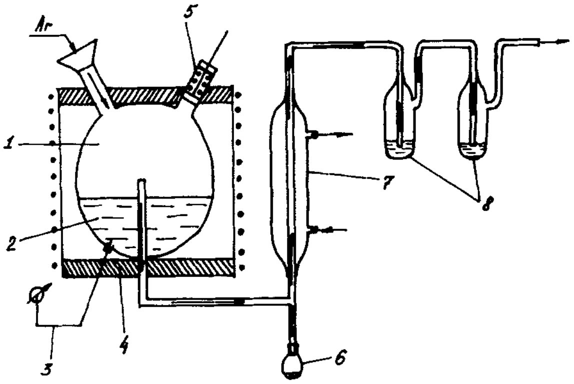


FIGURE 1 1—reaction vessel; 2—catalyst; 3—thermocouple; 4—electric heater; 5—rubber pusher; 6—ampule for products collection; 7—condenser; 8—Drecksel trap with Cd acetate.

determine the amounts of S-containing gases. The temperature of the vessel was maintained steady with the help of electric heater. The mass of catalyst was always approximately 20 times greater than the mass of pyrolyzed rubber, to exclude the drop of temperature in the reactor at the beginning of any pyrolysis experiment, and also to be sure, that the catalyst is not deactivated by the carboneous residue through several runs. Liquid products were collected into an ampule, and then weighted and analyzed on CHNOS-analyzer (model 11-06, Karlo Erba). The gases, coming with Ar through the Drecksel traps were collected, and then analyzed on the gas chromotograph (2 meter column of Poropak-Q). As a pyrolyzed material we used specially prepared vulcanized butadiene rubber with different S percent, and also raw butadiene rubber. The content of S in the vulcanized rubber was 1.7%, 2% and 2.3%, as in real rubber articles. The mass of rubber, pyrolyzed in one run was always about 1.5 g in pieces of about 1–3 mm long and 0.5 mm thick. We made about 10 runs on the 50 g of $NaAlCl_4$, and then changed the catalyst. The temperature of reaction vessel was varied from 300°C to 450°C. All experiments were carried out at fixed temperatures. The time of reaction was estimated visually, after the beginning of the run by pushing the rubber sample from the sample neck to the melt by the pusher.

The following runs were conducted in no less than 30 minutes after the previous one to exclude the mixing of pyrolysis products.

The results of such experiments are presented in Table I, concerning the yield

TABLE I

Yield of liquid products, weight percent

	Sulfur content in rubber			
T, °C	0%	1.7%	2%	2.3%
350	66	59	64	65
400	67	68	67	70
450	55	59	57	60

TABLE II

Composition of liquid products (elemental) weight % (±0.05%)

S-content in rubber, %		0	1.7	2.0	2.3
Temperature of pyrolysis, °C 400°	C	88.8	86.5	86	86
	H	10.4	10.4	10.4	10.4
	S	—	0.3	0.3	0.4
450°	C	90	87	87	86
	H	9.9	10.2	10.3	10.2
	S	—	0.3	0.3	0.4

of liquid products versus the temperature of catalyst and sulfur content in rubber.

One can see, that conversion of rubber into liquid products is practically independent on S-content. The maximum of yield occurs approximately at 400°C.

According to Ref. 3 in the presence of the catalyst $NaAlCl_4$ S-content in the products of the pyrolysis of oil fractions decreases. We also observed intensive S removal from rubber in the gaseous form (H_2S, etc.). In Table II there are presented elemental compositions of liquid products of pyrolysis.

When rubber with 1.7% of S was pyrolyzed at 450°C on quartz liquid products contained 86% of C; 10.3% of H and 0.6% of S.

In Table III there is presented yield of H_2S. We determined what percent of initial S in rubber, was removed as H_2S under different conditions.

Analysis on chromato-mass spectrometer "Hitachi" showed, that liquid products contained unusually high amounts of aromatic compounds: benzene, toluene, styrene, etc., and also some alkenes. One can also see, that C/H ratio in the products also indicates the presence of high amount of aromatics (C/H 9). Analysis of the gases, collected during pyrolysis, after H_2S absorption, showed the presence of mainly C_2 and C_4 gases.

Conversion to the gases is about 8–10% at 400°C and about 15% at 450°C.

So the catalyst $NaAlCl_4$ can effectively pyrolyze vulcanized S-containing rubber and produce liquid products with low S content, because of selective S-removal in the H_2S form. The total mass balance of pyrolysis can be presented in the following form.

TABLE III

Conversion of S in rubber to H_2S, weight %

S-content, % in rubber	1.7	2	2.3
Temperature			
350°C	25	27	26
400°C	32	32	33
450°C	39	38	41

100% vulcanized rubber	60–70% liquid products	+	10%–15% gases	+	15–20% residue on catalyst
100% sufur in rubber	8–10% liquid products	+	30–40% gases (H_2S)	+	50–60% (residue)

As another interesting S-containing model we chose the solution of *n*-dioctilsulfide in pentadecane of 0.15–0.20 g/g concentration. We also studied the pyrolysis of this system on $NaAlCl_4$.

It is well-known from literature, that Lewis acids ($AlCl_3$, BF_3, $AlBr_3$, $TiCl_4$, $SbCl_3$, $GeCl_4$, etc.) easily form complexes with S-containing compounds in the different media.[3,4] We supposed, that our system was quite similar in this respect. We succeeded in obtaining some results, which support this hypothesis.

The reaction of ($C_{16}H_{34}S$—$C_{15}H_{32}$) mixture in the media of $NaAlCl_4$ at atmospheric pressure and temperatures in the range 200–240°C was studied with the help of special apparatus (Figure 2). The melt of $NaAlCl_4$ was placed in the preheated reactor with the reactive mixture ($C_{16}H_{34}S$—$C_{15}H_{32}$) at an appropriate temperature. The system consisted of two separate liquid phases, because of the

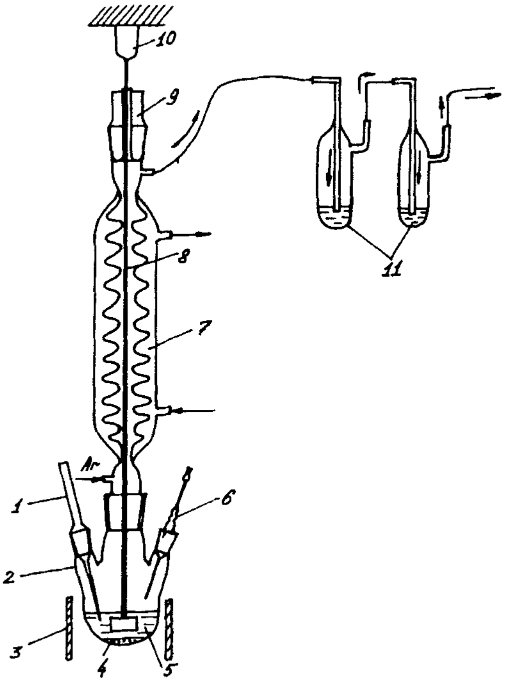


FIGURE 2 1—thermocouple; 2—vessel; 3—heater; 4—catalyst; 5—reactive mixture; 6—a special neck for analysis; 7—cooler; 8—stirrer; 9—stirrer inlet; 10—electromotor for stirrer; 11—Drecksel traps.

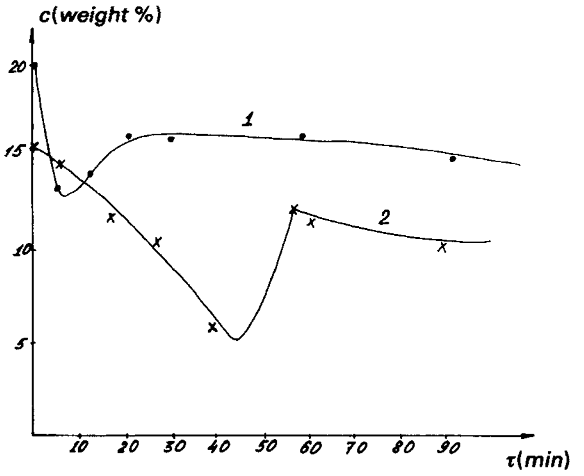


FIGURE 3 Concentration of sulfide versus time of reaction. 1—$t = 210°C$, 2—$t = 235°C$.

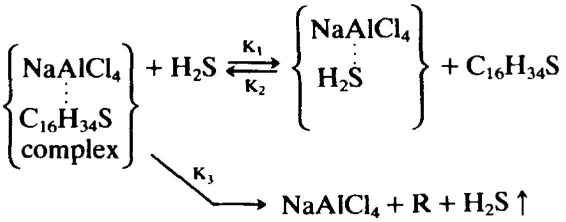
densities difference. To make a sufficient surface of contact between the catalyst and reactive mixture, the mechanical stirrer mixed the reagents at a steady speed of rotation. The reaction time was counted from the moment of catalyst introduction. The temperature of vessel was controlled by thermocouple and maintained constant during each experiment. The experiments were conducted under steady Ar flow of 1 cm^3 per second. During the experiment the samples of the hydrocarbon phase could be taken through the special neck of the Vessel with the help of a syringe with a long needle. Then the samples were analyzed on the cromatograph (3 m of SE-30 column) and chromato-mass spectrometer. Gases produced in the reaction came through the Drecksel traps with the solution of Cd acetate to determine the amount of H_2S.

The catalytic reaction produced gaseous H_2S and also some hydrocarbons, which did not contain S. S content in the liquid hydrocarbon phase could drop in 1.5–2.5 times in an experiment. The kinetic curves of ($C_{16}H_{34}S$) concentration are presented in Figure 3. One can see, that there is prominent minimum, whose interpretation is quite problematic.

The concentration of ($C_{16}H_{34}S$) was determined cromatographically in the hydrocarbon phase. So, it is probable, that the reason of the sulfide concentration decrease is not only its transformation to hydrocarbons and H_2S, but also its forming the formation of complexes on the catalyst. Really, it was possible to observe the sulfide concentration drop about 5–15% per day even at room temperature, when the reactive mixture was brought into the contact with unmelted catalyst. Under these conditions we did not observe H_2S appearance at all.

More strange thing is the following increase of sulfide concentration (Figure 3) in time. One can look at it in the following way.

The reaction of $C_{16}H_{34}S$ on the $NaAlCl_4$ goes through some intermediate complex

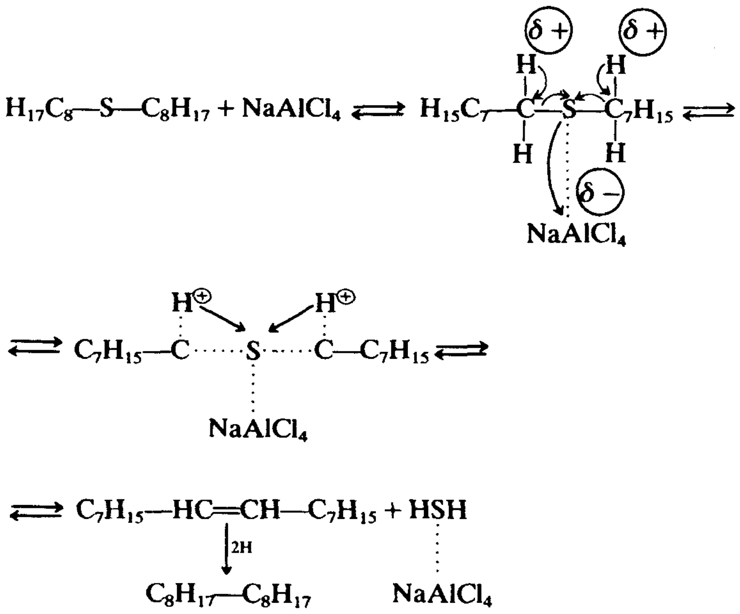


Such a scheme shows, that there is some equilibrium between NaAlCl$_4$ complexes with sulfide and H$_2$S.

H$_2$S is obtained from the complexes with sulfide. So, at first, when all the active sites in the melt of catalyst are free, the concentration of sulfide drops. Then there is sufficient amount of H$_2$S in the solution and it can take some vacant places on the catalyst surface and in the bulk, and the concentration of sulfide in the catalyst phase can decrease, while its concentration in the hydrocarbon phase can grow.

After sufficient time, due to the H$_2$S removal with Ar flow, its concentration on the catalyst surface can again decrease, and the sulfide concentration can also drop again.

The analysis on chromato-mass spectrometer of hydrocarbon phase after the reaction showed, that in the products of C$_{16}$H$_{34}$S destruction there was present mainly C$_{16}$H$_{34}$ paraffin, and also some lighter paraffins. We believe, that olefin, produced from C$_{16}$H$_{34}$S is quickly hydrated on NaAlCl$_4$ by H from the paraffin media of the mixture.



Our hypothetic model is in good accordance with Ref. 5, where the authors studied reactions of sulfides and mercaptans on $AlCl_3$.

Probably, the S-removal from rubbers happens in a similar way. It is also clear, that a lot of experimental work should be done to clarify this question.

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