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The polymerization of acetylene on catalysts having the composition titanium tetrabutoxide/organomagnesium or organolithium compounds

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Summary

The polymerization of acetylene was investigated using catalysts in which the titanium component, $Ti(OBu)_4$, was reduced with organomagnesium and organolithium compounds. In some cases, mainly with RMgBr, homogeneous films possessing good mechanical properties were obtained. The content of the trans-form of polyacetylene (40-80%) depended only vaguely both on the type of the reducing agent and on the reaction conditions. In all cases the film density was higher than that of films prepared according to Shirakawa.

Introduction

The unpleasant properties of polyacetylene, $(CH)_x$, and particularly its low oxidation stability, low polymerization yields related to the amount of the catalyst, insolubility and infusibility, are a serious obstacle to its application and investigation (1). At present, attention should therefore be concentrated on the preparation of new types of polyacetylene in which at least some of these disadvantages could be removed or restricted.

In our preceding study (2) we described a readily reproducible synthesis of $(CH)_x$ films using titanium tetrabutoxide/ethylmagnesium bromide ($Ti(OBu)_4$/EtMgBr) as the catalyst. In the dry state these films possess very good mechanical properties, which approach those of polypropylene, and a high density, close to the theoretical value (0.9-1.05 g/cm^3). Due to the high density the diffusion of oxygen into the bulk of the film is considerably slowed down. After exposure in the air during 8 months only the surface layer several µm thick was oxidized; the inner part of the film preserved its "metallic" character and after doping with iodine had virtually the same conductivity as freshly prepared samples.

It is known that in the case of Ziegler-Natta catalysts the polymerization course is markedly (and unpredictably) affected both by the catalyst composition and by a number of other factors. This study is therefore concerned with catalytic systems in which the $Ti(OBu)_4$ reducing component were some organomagnesium and organolithium compounds.

Experimental Part

30 min. after mixing of solutions of catalytic components in a flat-bottom reactor (or after their cooling to 195 K) pure dry acetylene was introduced into the space above the catalytic mixture (for composition see Table 1). The polymerization time was 30-40 min. Decomposition and extraction of the catalyst and isolation of the polymer were carried out using a methanol/ acetic acid mixture (10:1 by vol.), similarly as described in (2). All operations were performed in an argon atmosphere.

The ash was determined by burning the samples in a platinum crucible. If possible, the IR spectra were recorded on free standing films, otherwise the KBr techniques was used.

Results and Discussion

Experimental results summarized in Table 1 are commented briefly below.

Catalysts with the organomagnesium reducing component

The only quantity which markedly depends on the length of the alkyl chain in RMgX is the relative yield (which increases with the length of R). However, similarly to all the syntheses of $(CH)_x$ described so far, the yields obtained using the catalytic systems investigated in this study are also very low. It seems that two-component systems with $Ti(OBu)_4$ are not sufficiently active in the polymerization of acetylene. The route towards higher yields might perhaps lead via multicomponent catalytic systems containing promotors and activators.

The nature of the halogen atom in RMgX predominantly affects the quality of the product. RMgBr give films with the best mechanical properties. With RMgCl the films obtained are rather brittle. RMgJ are the least suited compounds for use as the catalytic component. Diethylmagnesium, which gave only a small quantity of red polyacetylene powder (obviously having a low molecular weight), was also studied. The easiness of catalyst decomposition and extraction also depends on the nature of the halogen atom. With RMgCl the washing out of the catalyst was very difficult, and the ash content could not be reduced below 5% by employing the procedure just mentioned.

The effect of polymerization temperature is rather unclear. With some catalysts low temperature supports the polymerization (EtMgBr, MeMgJ,BuMgCl,CeMgBr), with others the effect is an opposite one (EtMgJ, Et_2Mg). The temperature which with Shirakawa's system $Ti(OBu)_4/Et_3Al$ has a decisive influence on the content of both isomers in the polymer is of no great importance here.

Similarly to Shirakawa's system (3), in these cases too the quality of the product markedly increases with increasing catalyst concentration. At $[Ti(OBu)_4] < 0.05$ mol/l, only powder $(CH)_x$ or a little cohesive gel is always formed. At high catalyst concentrations the catalytic mixture often becomes completely solidified, which however does not impair its good activity in the polymerization.

Virtually in all cases the optimal molar ratio of the

Table 1

Polymerization of acetylene on catalysts of the type $Ti(OBu)_4$/organometallic magnesium or lithium compounds

Reducing agent	Solvent	$[Ti(OBu)_4]$ mol/l	Optimal[a] ratio [MI]:[TI]	Temperature K	Type[b] of catalytic mixture	Type[c] of polymer formed	Relative yield[d]	Content[e] of trans-form %	Length[f] contraction %	Density[g] g/cm^3
EtMgBr[h]	ether	0.22	2÷3	298	h	gb	0.18	60		
				195	o	fb	0.19	43	40	0.9÷1.0
EtMgJ	ether	0.20	2÷3	298	h	fb	0.15	75	20	0.8÷0.9
				195	p	p	~0.01			
Et_2Mg	ether:dioxan 1:3 mixture	0.09	2÷4	298	h	p	0.05			
				195	c	p	~0.02			
MeMgJ	ether	0.20	2÷6	298	h	p	~0.01			
				195	p	fs	0.08	60	5	0.5÷0.7
BuMgBr	ether	0.20	2÷3	298	h	gs	0.19	65		
				195	o	fb	0.21	45	40	0.8÷1.0
BuMgCl	ether	0.22	2÷3	298	s	fb+g	0.15		25	0.5÷0.7
				195	s	fb	0.35	50	40	0.7÷0.8
OcMgCl[i]	ether	0.20	2÷4	298	s	fb+g	0.85	70	20	0.6÷0.8
				195	s	g	0.90	45		
CeMgBr[j]	ether	0.20	2÷3	298	s	fb	1.00	60	40	0.7÷0.9
				195	s	fb	1.45	40	40	0.7÷0.9
n-BuLi	hexane	0.16	2÷4	298	p	fb	0.20	50	30	0.7÷0.9
				195	p	fb	0.20	40	35	0.7÷0.9
sec-BuLi	hexane	0.18	2÷6	298	h	gs	0.10	70		
				195	h	p	~0.01			
PhLi	ether	0.16	>5	298	h	fb	0.08	45	40	0.6÷0.8
				195	p	p	~0.01			
$LiAlH_4$	tetrahydrofuran	0.04	>2	298	h	gb	~0.03	40		
				195	h	p	~0.01			

[a] M - magnesium or lithium. [b] h - homogeneous solution; o - solution with oily sediment; p - solution with precipitate; c - crystalline precipitate; s - solid mixture. [c] p - powder; gs or fs - gel or film on the surface; gb or fb - gel or film on the reactor bottom. [d] Relative yield is given in g/g $Ti(OBu)_4$. [e] Calculated from IR spectra using Shirakawa's relation (3). [f] Irreversible contraction of the film during drying. [g] Density of dry film calculated from dimensions and weight. [h] Cf. (2). [i] Octylmagnesiumchloride. [j] Cetylmagnesiumbromide.

catalytic components varies in the range [Mg]:[Ti] = 2÷4. MeMgJ is an exception, since its reducing effect for $Ti(OBu)_4$ is distinctly lower, and it also gives a low-quality product.

During drying, in all cases the effect observed was the same as with the system $Ti(OBu)_4$/EtMgBr (2): the film was irreversibly and anisotropically reduced in volume and its length contraction was always smaller than thickness contraction. In some cases the films possess high density close to the theoretical value. In the swollen state, however, they obviously have a high specific surface area, so that they are well suited for application in electrochemical cells.

Catalysts with organolithium reducing component

As a rule, products obtained using catalysts containing an organolithium component do not attain the quality of films prepared with Grignard reagents. Films possessing satisfactory mechanical strength were obtained only with n-BuLi. The relative yields are rather low. In all cases under investigation a decrease in temperature results in a decrease in the rate of polymerization.

Conclusion

The results reported above show that high-quality $(CH)_x$ films are best synthesized using catalysts containing RMgBr. The products thus obtained possess high density and very good mechanical properties.

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