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Preparation and Properties of Polyallenes.
II. Phase Transitions of Polyallene

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Summary

Polyallenes prepared with the aid of organoaluminum–$VOCl_3$ catalysts appear to exist in three distinct phases: two crystalline phases (I and II) and an amorphous phase. Phase I shows two strong X-ray diffraction peaks at d = 5.62 Å and d = 4.04 Å; phase II has three strong peaks at d = 6.28 Å, d = 5.03 Å, and d = 4.21 Å. The band of the amorphous phase has its maximum at about d = 5.6 Å.

In polymers prepared at room temperature, phase I predominates. At higher temperatures of polymerization the amount of phase II increases markedly, at the expense of phase I. At very low polymerization temperatures (< 0°C), mainly amorphous polymers were obtained. Heat treatments (75–120°C) of the polymers in many solvents (e.g., heptane, tetralin), resulted in a decrease of phase II. In boiling cyclohexane or benzene, on the other hand, a distinct partial conversion of phase I into phase II was noticed.

X-ray investigation of a solid sample at increasing temperatures showed that phase II is converted into phase I in the temperature range 95–115°C. Upon lowering the temperature, no formation of phase II took place. It was concluded that (1) at increased polymerization temperatures phase II is formed more rapidly than phase I; (2) in the absence of solvents, phase II is metastable with respect to phase I; and (3) in the presence of cyclohexane and benzene, phase II is more stable than phase I; in many other solvents phase I is the more stable form.

In the preceding paper [1] the polymerization of allene induced by Ziegler-type catalysts has been described. The polymers appeared to be linear and generally highly crystalline. In the present paper, the physical structure of the polymers in relation to polymerization conditions and to thermal and solvent treatments is discussed.

INVESTIGATION OF THE PHYSICAL STRUCTURE

The crystallinity of the polymers was investigated at powders by means of X-ray diffraction. Most of the polymers investigated appeared to be crystalline for the greater part. Further study revealed that in polyallene generally two crystalline phases occur. The one phase (phase I) has two intensive lines at d = 5.62 Å and

TABLE 1. Powder Diagram of Polyallene

Phase I[a]			Phase II[a]		
2θCuKα, deg	d, Å	Int.	2θCuKα, deg	d, Å	Int.
14.1	6.28	ww?	14.1	6.28	s
15.8	5.62	ss	17.6	5.03	s
17.6	5.03	ww?	21.2	4.21	m
22.1	4.04	s	25.4	3.51	w
25.5	3.49	ww	27.0	3.30	w
27.8	3.21	ww	29.0	3.08	w
29.5	3.03	ww	31.6	2.83	w
31.8	2.81	w	34.1	2.63	w?
34.0	2.63	m	35.4	2.53	w
36.2	2.48	w	35.6	2.52	m
39.5	2.28	ww	36.5	2.46	ww
42.5	2.13	ww	39.4	2.29	mw
44.7	2.03	w			
47.0	1.93	ww			
50.8	1.80	ww			
52.1	1.75	ww			

[a] d, interplanar spacing; 2θ, diffraction angle; Int, intensity; s, strong; m, moderate; w, weak; ss, very strong; ww, very weak; mw, moderately weak.

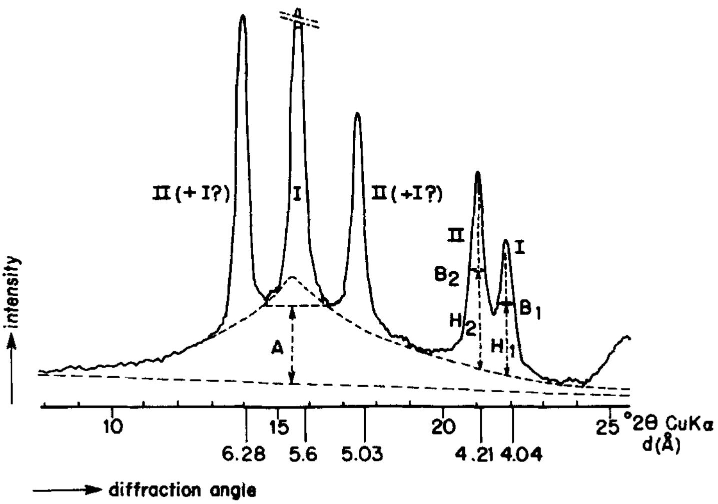

FIG. 1. X-ray photometer trace of linear polyallene.

d = 4.04 Å (diffraction angles 2θ 15.8° and 22.1°, respectively); the other phase (phase II) has three strong lines at d = 6.28 (14.1° 2θ), d = 5.03 (17.6° 2θ) and d = 4.21 Å (21.2° 2θ). The diagrams always displayed an amorphous band at d = 5.6 Å (16° 2θ). See Table 1 and Fig. 1.

In most of the polymers prepared according to the procedures given in Part I [1], phase I predominated. On further investigation, however, it was found that the physical structure of the polymers could be influenced by a proper choice of reaction conditions during the synthesis, or by subjecting the polymers to heat treatments. To express this we introduce two index numbers: II/I as a measure for the ratio of the quantities of phases II and I, and A/C as a measure for the ratio of amorphous to crystalline material.

For the determination of the II/I number, the ratio of the surface of the peak at 21.2° 2θ to that at 22.1° 2θ has been taken (Fig. 1). For determination of the A/C value, we have taken the amorphous band at 16° 2θ as a measure for the quantity of amorphous material. The top of this band cannot be measured, because it is covered by the strongest line of phase I. Instead of the surface of the amorphous band, for practical reasons, height A (Fig. 1) is taken as a measure for the intensity; it is the half sum of the heights at 14.7° and 16.9°.

As a measure for the crystalline fraction, the surface of the peak at 22.1° 2θ of phase I is taken, calculated as $H_1 \times B_1$. The contribution of phase II to the crystalline fraction has not been included in the calculation. This procedure is acceptable as long as the content of phase II is low. For higher contents of phase II, the contribution of phase II to the total crystallinity becomes more important. The true ratio of amorphous/crystalline is then smaller than A/C. The A/C figure has been calculated as $10A/(H_1 \times B_1)$.

It may be clear that this manner of quantitative interpretation presents only a rough approximation. The measurements at low and very high contents of amorphous material may cause an error of about 10% in the A/C value. For very low II/I ratios, measurement of the peak at 21.2° 2θ is very inaccurate, because it disappears in the foot of the peak at 22.1° 2θ. This is also the case when both lines are broadened. This procedure appeared to be sufficiently adequate, however, for the present investigation.

Influence of Reaction Conditions on II/I and A/C

Most of the polymers investigated have II/I values of 0.07–0.15 and A/C values of 0.20–0.40. In general there is a tendency to an increased A/C value when the viscosity of the polymer formed is low. The polymerization temperature has a distinct influence on the physical structure of the polymer. The polymerization experiments of Fig. 2, which were carried out in heptane, show the amount of

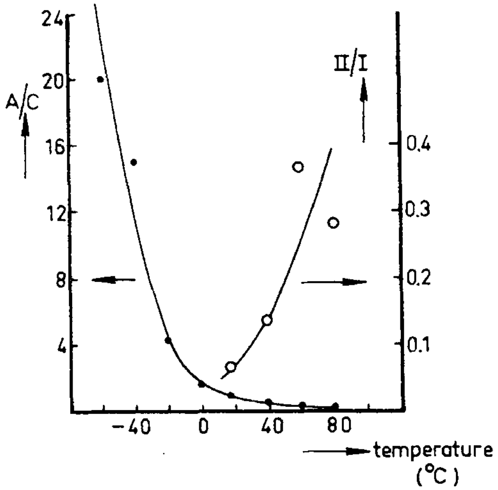

FIG. 2. Crystallinity of polyallene at varying polymerization temperatures (●, A/C; ○, II/I; polymerization conditions: 300 ml of heptane, 10 g of allene, 0.35 mmole of $VOCl_3$, 3.2 mmole of $Al\text{-}i\text{-}Bu_3$, time 2 hr (−80° to −40°C) and 15 min (−40° to 80°C); see Fig. 3 of [1].

crystalline material to decrease at decreasing polymerization temperature. Between about −40 and −80°C an almost completely amorphous polymer was obtained. At higher temperatures (18–80°C), the II/I ratio appeared to increase. This effect was even much more pronounced when the polymerization experiments were performed in cyclohexane (Table 2).

TABLE 2. Relationship between Polymerization Temperature and Physical Structure of Polyallene
(600 ml of cyclohexane, 10 g of allene, 0. 5 mmole of $VOCl_3$, 4. 4 mmole of Al-i-Bu_3, time 15 min)

Temp. °C	Polymer, g	[η]	A/C	II/I
7	1. 1	6. 3	15	–
20	2. 7	7. 0	0. 70	0. 10
50	4. 9	10–11	–	6. 2

The physical structure can also be influenced by giving the polymers a heat treatment afterward. A completely amorphous polymer can be obtained by pouring a hot solution of the polymer in, e.g., monochlorobenzene on dry ice (see Fig. 3d). By treating the polymers with hot solvents, and then cooling slowly to room temperature, the crystallinity generally increases somewhat. The effect of this treatment on the II/I ratio is worth mentioning. Treatment of the polymers with solvents such as heptane, tetralin, decalin, trichloroethylene, and tetrachloroethane in the temperature range 75–120°C is accompanied by a more or less pronounced decrease of the II/I ratio. Surprisingly, however, a distinct transformation from phase I to phase II occurs when the polymers, at 80°C or slightly higher, are heated in the solvents cyclohexane and benzene. Accordingly, a polyallene sample with a II/I ratio of 0. 10, after a time varying from 10 min to 2 hr of contact with cyclohexane in a 100°C bath (nitrogen atmosphere), and thereafter cooled to room temperature at a rate of approximately 0. 4°C min, was found to have obtained II/I ratios between 3. 8 and 5. 7. By contrast, the II/I ratio of the sample was found to have dropped to 0. 05–0. 02 when the temperature treatment was effected under analogous conditions in heptane. In Figs. 3a–c, these II/I shifts are illustrated with reference to some examples.

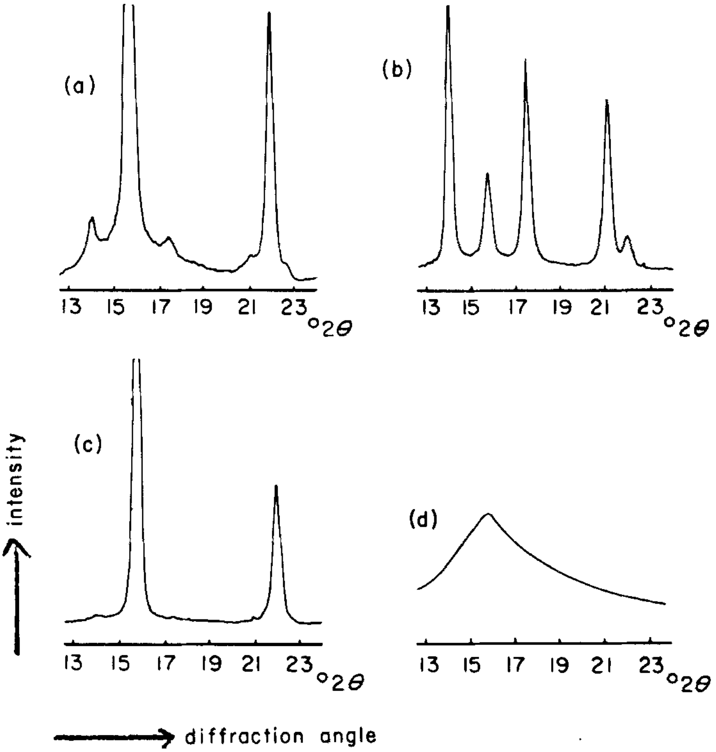

FIG. 3. X-ray photometer traces of polyallene: (a) untreated (II/I = 0.10); (b) refluxed for 20 min in cyclohexane, cooled slowly (II/I = 5.5); (c) refluxed 1 hr in heptane, cooled slowly (II/I < 0.02); (d) hot solution in monochlorobenzene quenched in dry ice.

Investigation at Elevated Temperatures

For a closer study of the processes that take place when polyallene is subjected to a heating and cooling cycle, the X-ray diffraction investigation was also performed at elevated temperatures. For this investigation, samples of a high II/I ratio were chosen. They were stabilized with Flexamine* to prevent oxidation. In a typical experiment a polymer sample was heated to 130°C, the temperature

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*Flexamine, an antioxidant fabricated by Naugatuck, is a reaction product of a diarylaminoketone and N, N'-diphenylparaphenylene diamine.

interval of 90–130°C being passed in about 6 hr. When the temperature had reached approximately 95–100°C, the amount of phase II decreased rapidly. At the same time the intensity of the peak at 22.1° 2θ increased, indicating a distinct conversion of phase II into phase I. This transformation proceeds up to 115°C, at which temperature phase II disappears practically completely. Upon raising the temperature further, the amount of phase I decreases due to melting. At 130°C the polymer has been melted completely. When the molten polymer was cooled, only phase I appeared to crystallize. In another typical experiment a polymer rich in phase II was heated to a temperature between 90 and 115°C, e.g., 107°C, and kept at this temperature for some time. The transformation of phase II into phase I appeared to stop practically instantaneously after reaching this temperature. When the temperature was lowered, no change in the II/I ratio was observed. Raising the temperature again, the transformation of II into I was resumed immediately after 107°C.

The results obtained in this investigation indicate that:

1. In the absence of solvents, phase II is metastable with respect to phase I. The transition of phase II into phase I in the 90–115°C range seems to take place via the melt with increasing temperature; phase II melts first, after which the melt recrystallizes in the presence of phase I, completely or partly as I.
2. At increased polymerization temperatures, phase II is formed more rapidly than phase I. This effect is independent of the solvent applied.

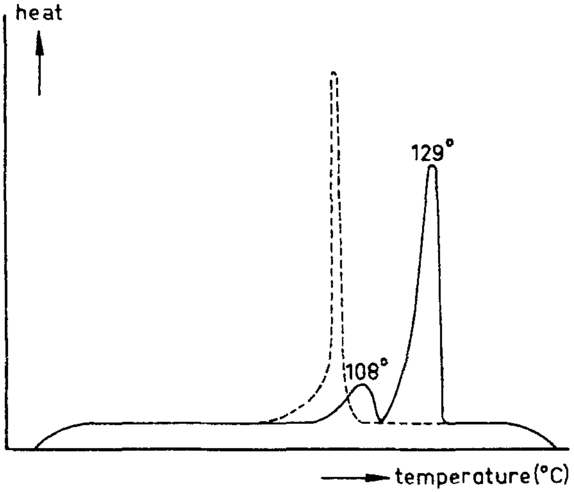

FIG. 4. DTA thermogram of polyallene (II/I = 5.6): ———, heat absorbed on heating; - - - - - -, heat released on cooling (heating and cooling: rate 27°C/hr; antioxidant Flexamine).

3. In the solvents cyclohexane and benzene, phase II is more stable than phase I; in many other solvents, such as heptane, tetralin, decalin, trichloroethylene, and tetrachloroethane, phase I is the more stable form. The change of the II/I ratio in cyclohexane and in heptane by a factor of about 300 corresponds energetically with approximately 3 kcal. Apparently the solvation energies involved in these transformations differ markedly for these solvents.

Conclusion 1 is supported by data obtained in differential thermal analysis (DTA) studies. DTA thermograms of samples containing both phases usually showed two endothermic peaks: in the temperature ranges 101–108°C and 126–129°C, respectively (see Fig. 4). Melting of phase II is represented by the first peak; the second peak shows the melting of phase I. The magnitude of this peak corresponds to the amount of phase I originally present in the sample plus a contribution due to the transformation of II into I. When the molten sample was cooled, only one peak was found to return. The endothermic peak at 108°C seems to be rather low in comparison with the melt peak of phase I. The endothermic effect due to melting of phase II might be counteracted, however, by the exothermic effect due to recrystallization of the melt of phase II into phase I.

DISCUSSION

It was found in this study that polyallene can occur in two distinct crystalline forms and an amorphous form. No indications were obtained for the existence of a third crystalline form, as mentioned by Baker [2]. Baker concludes that all other types are metastable with respect to his type 1, which corresponds mainly to our phase II. By contrast, our results strongly indicate phase I to be the more stable phase under most conditions. It could be transformed into phase II only under very special conditions of solvent and temperature. It has been checked that these transitions are of a physical origin: no relation was found between the II/I ratio and the chemical structure (content of vinyl and cis [1]) of the polymers.

EXPERIMENTAL DETAILS

The heat treatments of the polymers were carried out in test tubes containing 20 mg of polymer and 15 ml of organic solvent in a nitrogen atmosphere. They were kept at constant temperature in a thermostated oil bath. After a certain time, heating was stopped and the bath was left to cool. The polymer was isolated by decantation of the solvent or by centrifugation. It was dried in vacuo over phosphorus pentoxide.

The X-ray investigations at room temperature were carried out with a Nonius fourfold focusing Guinier-type camera [3], using CuKα radiation. Tube Cu, 40 kV, 21 mA, 1 hr, line focus. The intensities were measured with a microdensitometer. A modified Philips diffractometer was used for the work at elevated temperatures. The sample was mounted in a small oven and investigated in transmission A curved-crystal monochromator behind the sample focused the divergent diffraction beam into a slit before a proportional counter [4]. The recorder charts were used to measure the intensities.

The DTA measurements were performed in a DTA apparatus developed by the Technical Physics Department of TNO and the Technical University of Delft. In this apparatus, small heat-flow meters were applied with which a heat flow of 0. 2 μ-watt can be detected [5]. Measurements were carried out at samples of about 10 mg under nitrogen. To reduce decomposition it appeared necessary to add a stabilizer. Of the stabilizers investigated, Flexamine was chosen for this work, because it had no peaks in the temperature range studied.

Acknowledgments

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Zusammenfassung

Polyallene hergestellt mit Al-i-Bu_3-$VOCl_3$ Katalysatoren zeigen 3 unterschiedene Phasen und zwar zwei kristalline Phasen (I und II) und eine amorphe Phase. Phase I zeigt zwei stark Maxima in das Röntgeninterferenzbild bei d = 5. 62 Å und d = 4. 04 Å; Phase II hat drei starke Maxima bei d = 6. 28 Å, d = 5. 03 Å, und d = 4. 21 Å. Die amorphe Phase zeigt ein Maximum bei d = 5. 6 Å. Sowohl das Verhältnis Amorph/Kristallin als das Verhältnis Phase I/Phase II ist abhängig von der Polymerisationstemperatur. Ausserdem kann das Verhältnis Phase I/Phase II beeinflusst werden durch Behandlung mit verschiedene Lösungsmittel und durch Wärmebehandlung des Polymeres.

Résumé

L'étude aux rayons-X de polyallène preparé avec l'initiateur Al-i-Bu_3-$VOCl_3$ démontre qu'il y a trois phases distinctes, à savoir deux phases cristallines (I et II) et une phase amorphe. La phase I fait voir dans la diagramme de rayons-X deux maximums à d = 5.62 Å et à d = 4.04 Å, tandis que la phase II démontre trois maximums à d= 6.28 Å, à d = 5.03 Å, et à d = 4.21 Å. La phase amorphe a une bande à d = 5.6 Å. Le rapport amorph/cristallin, aussi que le rapport Phase I/Phase II dépendent de la température de la polymérisation et de traitement thermique de la polymère. En outre le rapport Phase I/Phase II peut être effectué par traitement avec des solvants divers.