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The Initiation of Vinyl Polymerization by a Model Peroxy Ester

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(Eingegangen am 8. Februar 1961)

SUMMARY:

The fully acetylated di-peroxy ester of mucic acid was used to initiate the polymerization of styrene, and 84% of the theoretical amount of CO_2 was collected. Treatment with base did not affect the intrinsic viscosity of the resulting polymer. When this saponified polymer was subsequently oxidized by lead tetraacetate, its intrinsic viscosity showed a decrease. It is concluded that the peroxy ester showed a concerted split of the O-O and C-C bonds during the initiation and that the alkoxy counter-radical is quite inactive towards polymerization.

ZUSAMMENFASSUNG:

Um einen Einblick in den Initiierungsmechanismus von Perestern zu erhalten, wurde Styrol mit dem vollständig acetylierten Diperoxyester der Schleimsäure polymerisiert. Dabei wurden 84% der theoretischen Menge an freigesetztem CO_2 erfaßt. Wird das erhaltene Polymere mit Basen behandelt, so tritt kein Abfall der Viskositätszahl ein. Dies ist jedoch der Fall, wenn das verseifte Polymere mit Bleitetraacetat umgesetzt wird. Aus diesen Ergebnissen ist zu schließen, daß im Peroxyester während der Initiierung eine gemeinsame Spaltung von O-O- und C-C-Bindungen erfolgt, das entstehende Alkoxy-Radikal jedoch nicht polymerisierend wirkt.

Introduction

In 1955 HAHN and FISCHER¹) prepared poly(t-butyl-peroxyacrylate) from polyacryloylchloride and t-butyl hydroperoxide. The polymeric peroxy ester was used to initiate the polymerization of methyl methacrylate. SMETS et al.²) adopted this technique to prepare a copolymer containing t-butyl-peroxyacrylate and methyl methacrylate. When this polymeric peroxy ester was heated in dioxane solution it yielded CO_2 (decarboxylation) and acid groups (rearrangement and disproportion-

¹⁾ W. HAHN and A. FISCHER, Makromolekulare Chem. 16 (1955) 36.

²⁾ G. SMETS, A. POST, M. MULLIER, and J. P. BEX, J. Polymer Sci. 34 (1959) 287.

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ation). Work by BARTLETT, HIATT, PINCOCK, BENNING, RUCHHARDT, and SIMONS³⁻⁶ indicates that many simple peresters show a concerted cleavage at the C-C and O-O bonds when heated.

In order to investigate whether polymerization initiation by peresters takes place mainly through:

or through the alternate mechanism:

В.

it was deemed desirable to synthesize a simple model initiator. A di-peroxy ester would leave the initiator segment centered in the polymer chain. Saponification would degrade the chain if initiation takes place according to Scheme A. In the case that Scheme B is operative, initiation would yield carbon dioxide, and saponification would not reduce the molecular weight of the polymer chain. Degradation of the centered initiator segment would have to take place by some other means. If the initiator molecule has a glycol moiety incorporated in it, between the two perester groups, it could be degraded by lead tetraacetate. The di-peroxy ester of mucic acid fulfilled these requirements, and its fully acetylated form was accordingly synthesized from galactose.

Results and Discussion

When di-t-butyl tetra-O-acetyl peroxymucate (I), which had been prepared from galactose was used to initiate the polymerization of styrene, a polymer was obtained which was treated with base to

(CH₃)₃CO₃C-(CHOCOCH₈)₄-CO₃C(CH₃)₃ I

cleave all ester linkages. It was then oxidized by lead tetraacetate to cleave all glycol linkages.

⁸⁾ P. D. BARTLETT and R. R. HIATT, J. Amer. chem. Soc. 80 (1958) 1398.

⁴⁾ P. D. BARTLETT and D. M. SIMONS, J. Amer. chem. Soc. 82 (1960) 1753.

⁵⁾ P. D. BARTLETT, E. P. BENZING, and R. E. PINCOCK, J. Amer. chem. Soc. 82 (1960) 1762.

⁶) P. D. BARTLETT and R. E. PINCOCK, J. Amer. chem. Soc. 82 (1960) 1769.

The intrinsic viscosity, which was virtually unaffected by the base treatment, showed a marked decrease upon the lead tetraacetate oxidation.

During the polymerization of the styrene, initiated by the di-peroxy ester I, all off-gases were collected and analysed for carbon dioxide, and 1.68 moles of CO_2 was collected per mole of I (84 % of theoretical amount). From these data the main reaction in this initiation and subsequent degradation seems to be:

	$\mathbf{I} \stackrel{\Delta}{\rightarrow} 2$	$2 CO_2 + 2 CO_2$	•OC(CH ₃) ₃ +	HĊOCOCH ₃ (HCOCOCH ₃) ₂ HCOCOCH ₃
polymer 2 HC=O + 2 HCOOH	Pb(OAc)4	polymer (HCOH)4 polymer	€ OCH3-	↓ monomer polymer HCOCOCH ₃ (HCOCOCH ₃), HCOCOCH ₃ polymer

Since the intrinsic viscosity of the base treated polymer had not decreased, it was concluded that little initiation of the type

$$\begin{array}{cccc} & & & & & & & & \\ CO_{3}C(CH_{3})_{3} & & & & C & & & \\ (CHOCOCH_{3})_{4} & & \Delta & & (CHOCOCH_{3})_{4} & & M & (CHOCOCH_{3})_{4} \\ \hline CO_{3}C(CH_{3})_{3} & & & C & & C & -O - \\ & & & & & & O \end{array}$$

had taken place, as the initiator would then occupy the center of the polymer and be connected to the polymeric chains by ester linkages.

An attempt to interpret quantitatively the values obtained for intrinsic viscosities before and after lead tetraacetate oxidation (0.58 and 0.36 respectively) lead to the following considerations: Assuming reactivity ratios for the radicals:

in the reaction:

I
$$\xrightarrow{\text{Monomer}}$$
 II $\xrightarrow{\text{polymer}}$ + 2 III-polymer + 2 CO₂ \uparrow

it became possible to calculate the corresponding ratios for both number (M_n) and weight (M_w) average molecular weights before (M_1) and after (M_2) glycol cleavage. The only distribution assumed was the one due to the higher molecular weight of the polymer initiated by II as compared to the one initiated by III, the relative amount of these two fractions being controlled only by the assumed reactivities of the radicals II and III. In this manner a theoretical curve could be obtained (Fig. I).



Fig. 1. Theoretical relationship between the ratio of the molecular weights of polystyrene before (M_1) and after (M_2) initiator-specific cleavage, and the reactivity ratio of radicals II and III

Using the STAUDINGER-KUHN equation $[\eta] = K \cdot M^a$ with a = 0.74 for polystyrene in benzene⁷, the ratio of the viscosity average molecular weight before and after glycol cleavage of the polymer is 1.84. When this is fitted into the theoretical plot the two numbers obtained for the ratio of reactivities are: 6 (based on wt. average) and 12 (based on number average). The viscosity average molecular weight will yield an intermedi-

⁷⁾ R. H. EWART and H. C. TINGEY, 111th ACS Meeting, April, 1947, USA, Abstracts of Papers 4Q.

ate value, closer to 6. This figure is necessarily approximate, but not unreasonable. The electron donating power of the three methyl groups in III can be expected to decrease the free radical character of the odd lectron relative to II.

$$\begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \rightarrow O \\ \uparrow \\ CH_{3} \end{array}$$

The chain transfer constant for the styrene/benzene is small $(0.18 \cdot 10^{-5})$ and the value of the constant is also low for monomer/polymer transfer⁸, so that these reactions may in first approximation be ignored.

Experimental

Preparation of di-t-butyl tetra-O-acetyl peroxymucate

a) Tetra-O-acetyl-mucoyl dichloride

Galactose was oxidized with nitric acid to yield mucic acid, m.p. 211 °C.9).

Acetylation¹⁰ followed by recrystallization from ethanol yielded tetra-O-acetyl-mucic acid as white crystals, m.p. 247-248 °C.

The tetra-O-acetyl-mucic acid was converted to its di-acid chloride by phosphorus pentachloride dissolved in acetyl chloride according to the procedure of DIELS and LOF-LUND¹¹). The crystalline material after washing with heptane had a m.p. of 173.5–175 °C.,

Anal.: Found 17.2% Cl (calc.: 17.1% Cl)

b) Di-t-butyl tetra-O-acetyl peroxymucate

Tetra-O-acetyl-mucoyl dichloride (3 g.), t-butyl hydroperoxide (21 ml.) and pyridine (12 ml.), were shaken for 3 days. The mixture was left to evaporate in air, and the residue washed with water. It was partly soluble. For this particular batch the insoluble material was recovered, dissolved in chloroform and washed with aqueous saturated sodium bicarbonate. Washing with water, drying of the chloroform layer over calcium chloride followed by evaporation of the solvent yielded a white crystalline mass. The crude material was dissolved in a minimal amount of benzene and recrystallized by adding a small amount of heptane to yield hexagonal crystals of m.p. 129.8–131.5 °C.

Anal.: Calculated: 50.57% C 6.51% H Found: 50.81% C 6.89% H

The infrared spectrum showed no hydroxyl, and three peaks in the carbonyl region: 1790 cm⁻¹ (very strong), and a doublet: 1745 cm^{-1} (very strong) and 1757 cm^{-1} (strong).

⁸⁾ F. R. MAYO, R. A. GREGG, and M. S. MATHESON, J. Amer. chem. Soc. 73 (1951) 1691.

⁹⁾ F. J. BATES, Polarimetry, Saccharimetry and the Sugars, (US) National Bureau Standards Circular C440, Page 528.

¹⁰⁾ Z. H. SKRAUP, Mh. Chem. 14 (1893) 470.

¹¹⁾ O. DIELS and F. LOFLUND, Ber. dtsch. chem. Ges. 47 (1914) 2351.

Polymerization of styrene

The tetra-O-acetyl-di-t-butyl peroxymucate thus obtained (100 mg.) was dissolved in benzene (100 ml.) containing redistilled styrene (50 ml.). The flask was attached to a uronic anhydride determination apparatus, the traps filled with aqueous $BaCl_2/NaOH^{12}$). The system was swept with nitrogen for 1 hr. and then boiled under reflux while sweeping slowly with nitrogen. After 8 hrs., the reaction was terminated and the $BaCO_3$ collected, converted to Ba-iodate which was determined by the addition of iodide and acid, the free iodine being titrated with thiosulfate¹²). (Under identical conditions but for the addition of the di-peroxy ester, no $BaCO_3$ was obtained and 0.77 g. of polymer formed).

The di-peroxy ester-initiated polymer was purified by dissolution in benzene followed by precipitation into methanol. Yield 13.8 g. The intrinsic viscosity as determined in benzene solution was $[\eta] = 0.58$. The polymer (1.5 g.) dissolved in benzene (100 ml.) was mixed with an 0.1 N methanolic solution of sodium methoxide (20 ml.) and left overnight. The base was removed by four extractions with water. The benzene solution was dried (CaCl₂) and the polymer recovered from the solution after filtration. Its intrinsic viscosity in benzene solution gave a value of 0.61.

Polystyrene which had been treated with sodium ethoxide was dissolved in benzene and mixed with a 1% solution of lead tetraacetate which had previously been recrystallized from acetic acid/acetic anhydride (95/5), and left for several days. Excess lead tetraacetate was removed by shaking with ethylene glycol (1.5 hrs.) followed by extractions with water, aqueous acid, aqueous carbonate and finally again water. The wet benzene solution of the polymer was then precipitated into methanol and collected. Dissolution in benzene provided a small amount of black precipitate, which was removed by filtration. The intrinsic viscosity of this oxidized polystyrene in benzene was found to be 0.36.

Acknowledgement

Thanks are due to Mr. G. F. GOODLEY who did part of the experimental work.

¹²⁾ A. JOHANSSON, B. LINDBERG, and O. THEANDER, Svensk Papperstidn. 57 (1954) 41.