

Instituto De Plasticos Y Caucho (C. S. I. C.)
Juan de la Cierva, 3, Madrid-6 (Spain)

Acroleindiethylacetal: Reaction with Free Radicals and Copolymerization

Roberto Sastre, José L. Mateo, and José Acosta

(Received 1 March 1978)

SUMMARY:

The reaction between acroleindiethylacetal (3,3-diethoxypropene) and free radicals and the behaviour of this acetal in the free radical copolymerization with unsaturated monomers has been investigated. The decomposition of benzoyl peroxide and tert.-butyl peroxide in acroleindiethylacetal has been studied in the liquid phase. On the basis of the obtained products a mechanism is proposed which involves the abstraction of a hydrogen atom by a primary radical from a carbon atom which is adjacent to oxygen. We also tried to copolymerize the acetal with several conventional comonomers but copolymers were only obtained when acrylonitrile and maleic anhydride were used. The remarkably uniform composition of the copolymers from the acetal and maleic anhydride is explained through a donor-acceptor complex between the two monomers.

ZUSAMMENFASSUNG:

Die Reaktion zwischen Acroleindiäthylacetal und Radikalen sowie das Verhalten dieses Acetals bei der radikalischen Copolymerisation mit ungesättigten Monomeren wurde untersucht. Auf Grund der Ergebnisse wird ein Mechanismus vorgeschlagen, der die Abstraktion eines H-Atoms von einem dem Sauerstoff benachbarten C-Atom durch ein Radikal beinhaltet. Copolymerisationsversuche des Acetals mit verschiedenen Monomeren waren nur mit Acrylnitril und Maleinsäureanhydrid erfolgreich. Die bemerkenswert einheitliche Zusammensetzung des Acetal-Maleinsäureanhydrid-Copolymeren zeigt, daß die Reaktion über einen Donor-Akzeptor-Komplex verläuft.

Introduction

It has been reported that free radical and ionic homopolymerization of acroleindiethylacetal does not take place¹⁻³. Nevertheless, Davies and Kiby found out that heating aliphatic acrolein-acetals at 130–150°C in the absence of initiator in nitrogen atmosphere was sufficient to convert the acetals into

low molecular weight polymeric materials. Also, in the patent literature⁵⁻⁸, the formation of polymeric products from acrolein acetals with vinyl phenols, acrylonitrile and acrylamide is described.

The purpose of this work is to investigate the reaction between acrolein-diethylacetal and free radicals and, moreover, the behaviour of the acetal in the free radical copolymerization with other unsaturated monomers, all with the purpose to check the real possibilities for the synthesis of new copolymers in the polymer field⁹⁻¹⁵, which are mainly characterized by the presence of unsaturated acetal units along their backbones.

Experimental

Materials

Acroleindiethylacetal was prepared according to Hibbert's or Smith's method^{16,17}. The crude product obtained in about 90% yield was fractionally distilled until impurities detectable by gas chromatography were essentially removed. Maleic anhydride was purified by sublimation, stored in a desiccator under N₂-atmosphere and resublimed prior to use. The solvents and vinyl monomers used were purified in the classical way¹⁸ and distilled immediately prior to use. The free radical initiator, 2,2'-azobisisobutyronitrile (AIBN), was purified by recrystallization from absolute ethanol below 40°C in subdued light, with storage under vacuum in the dark at about -10°C. Other free radical initiators were used in their commercial form.

Polymerization

The copolymerization reactions were accomplished in sealed tubes under high vacuum atmosphere at preselected temperatures. The required amounts of the reactants were placed into the tube. The tube was then sealed after degassing by repeated freezing and thawing cycles. The polymer was isolated by precipitation-filtration and purified by a new reprecipitation. Finally it was dried in vacuum to constant weight. The copolymerization was allowed to proceed only to a very low yield (<10%) in one series of experiments.

Analysis

Runs to determine the intermediate and end products of the reaction between the acetal and free radicals were carried out by heating a solution of tert.-butyl peroxide

or benzoyl peroxide (10 mol-%) in the acetal in a reaction flask. The reaction flask was connected to a 20 cm Vigreux column, fitted to a glass-head containing a coldfinger reflux condenser, which was joined to a water-ice trap, a dry ice trap and a liquid nitrogen trap. The whole system was first purged with helium, and a slow stream of helium was maintained during the reaction. The reaction flask was heated to 120°C so as to maintain a slow reflux at the base of the vigreux column and the temperature in the glass-head did not exceed 30°C. After 5h of heating, the reaction flask was allowed to cool and the flow of helium was increased to ensure the complete transfer of volatile products to the traps. The contents of traps were transferred to an evacuated flask equipped with a serum-cup. The products were analyzed by means of gas chromatography (G. C.) and mass spectrometry (M. E.). The liquid fraction was separated and also analyzed by preparative gas chromatography. In this case the products were identified by trapping each fraction from the gas chromatography apparatus in a dry ice trap and by obtaining the IR and/or NMR spectrum of the condensate. The residual mixture contained in the reaction flask was distilled under reduced pressure and analyzed in the above indicated way. The identification of each separated product was confirmed by showing that the retention time in G. C. and the IR, NMR and M. E. spectra of the known material were identical to those of the unknown in the reaction mixture.

IR absorption spectra were carried out using a Perkin Elmer spectrophotometer, md. 457. The NMR spectra in a Perkin Elmer, mod. R-12 (60 MHz) using TMS as internal standard. Gas chromatography instruments used were Carlo Erba, Fractovap C and Perkin Elmer, mod. F-11 and F-21. The system gas chromatography mass spectrometry was also a Perkin Elmer, mod. 270 (80 C. V.) instrument. The molecular weights were determined by vapour pressure osmometry (Hitachi, mod. 115) using chloroform as solvent. The copolymer composition of the acrylonitrile-acetal pair was determined by nitrogen analysis. In order to determine the anhydride content, samples of maleic anhydride-acetal copolymers were titrated with sodium methoxide following the Fritz and Liski method¹⁹.

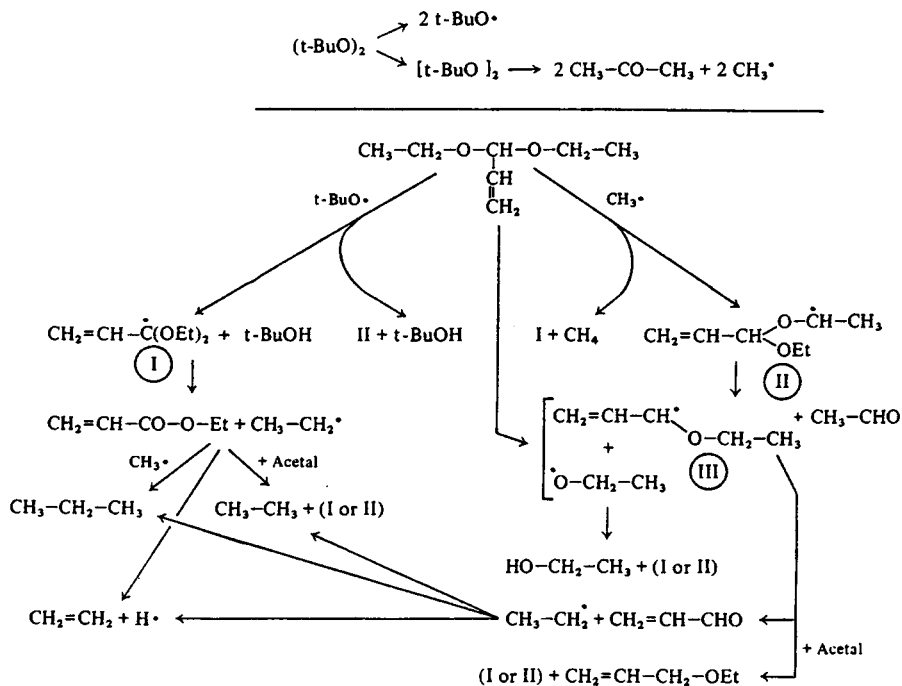
The equilibrium constant of donor-acceptor complexes between maleic anhydride and acetal was determined by the NMR method²⁰, using the shift of the singlet of maleic anhydride protons observed when the concentration of acetal was increased while the concentration of maleic anhydride was kept constant.

Results and Discussion

Reaction between acroleindiethylacetal and free radicals

The study on the reactivity of acroleindiethylacetal toward free radicals has been carried out using the alkoxy radicals which have been produced in the thermal decomposition of benzoylperoxide and tert.-butyl peroxide. The observed differences among the reaction products follow from the different compounds derived from the different peroxides. In order to achieve the

separation and identification of the complex reaction mixture, we used the techniques showed in the experimental part. The identified products are shown in Tab. 1. On the basis of the products formed a reasonable mechanism is presented in the following reaction scheme, which accounts for the experimental results and which is consistent with the known reactions of alkoxy radicals:



Among the identified products, tert.-butyl alcohol, acetone and methane are generated from tert.-butoxy radicals either by hydrogen abstraction from the acetal or by decomposition to yield methyl radicals and acetone. These results agreed with those obtained in the studies on decomposition of tert.-butyl peroxide²¹.

The abstraction of a hydrogen atom from a carbon atom which is adjacent to an oxygen atom, by tert.-butoxy or methyl radicals, leads to the radicals I and II. This lability or susceptibility to the transfer of hydrogen atoms on carbon adjacent to oxygen, has also been widely demonstrated in the literature. In the present case such lability is confirmed by the high ratio of the relative intensity between peaks $M-1$ and M in their mass spectra,

Tab. 1. Products from the reaction of t-butyl peroxide radicals with acroleindiethylacetal.

Compound	Identified by
Methane	G. C. comparative, M. E.
Ethylene	G. C. comparative, M. E.
Ethane	G. C. comparative, M. E.
Propane	G. C. comparative, M. E.
Acetaldehyde	G. C., IR, NMR
Ethyl alcohol	G. C. comparative, IR
Acrolein	G. C. comparative, IR
Acetone	G. C. comparative, IR
tert.-Butyl alcohol	G. C. comparative, IR
Allylethylether	G. C., IR, NMR
Ethyl acrylate	G. C. comparative, IR
Polymer	IR, NMR, \bar{M}_n

also in agreement with their chain transfer constant determined in the radical polymerization of styrene (see below).

Radical I decomposes to give ethyl acrylate and an ethyl radical. Radical II decomposes to give acetaldehyde and radical III, which at the same time decomposes to give acrolein and an ethyl radical. Such a radical III can be formed likewise by direct cleavage of acetal, which also involves the formation of the ethoxy radical. All the free radicals present in the reaction medium, can initiate the polymerization of unsaturated compounds or grow through the formation of simple organic compounds. In this way, the abstraction of a hydrogen atom by radical III gives rise to allylethylether; while ethane,

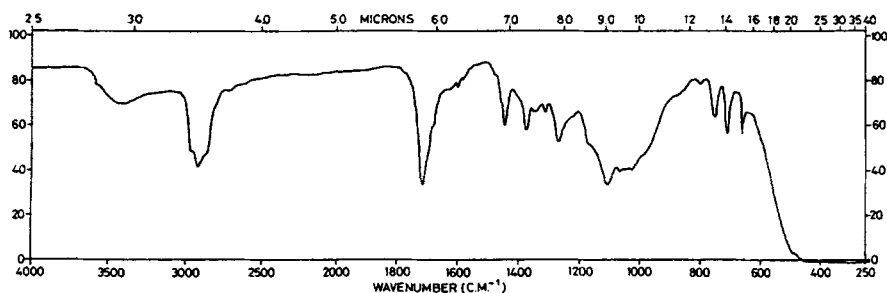


Fig. 1. IR spectrum of the polymeric product obtained from acroleindiethylacetal in a free radical medium.

methane and tert.-butyl alcohol are obtained through ethyl, methyl and tert.-butoxy radicals respectively. Propane is formed by the combination of methyl and ethyl radicals. The polymeric material obtained consists of units corresponding to the unsaturated compounds formed, as it follows from their IR and NMR spectra as shown in Fig. 1 and 2.

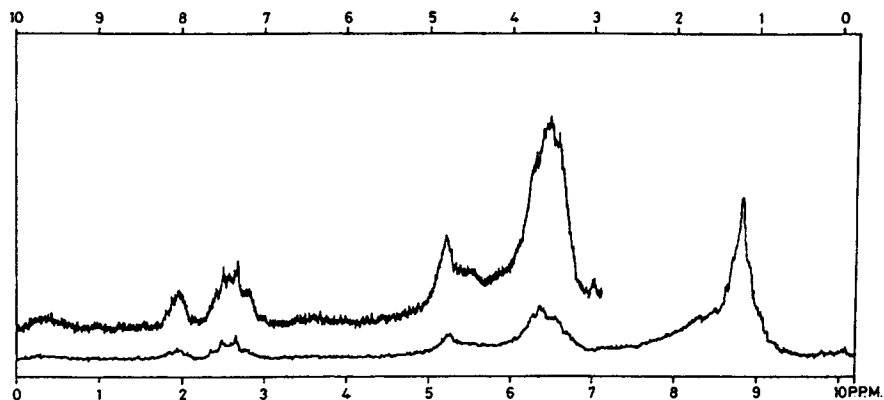


Fig. 2. NMR spectrum of the polymeric product obtained from the decomposition of benzoyl peroxide in acroleindiethylacetal ($\tau=2-2,5$ ppm. assigned to the aromatic protons of the benzoyl peroxide rest).

The vapour phase osmometry molecular weight determination revealed a number average molecular weight of 785.

Copolymerization

In order to establish the possibilities of copolymerization of acrolein diethylacetal, we tried to copolymerize it with several conventional comonomers. Copolymers were only obtained when acrylonitrile and maleic anhydride were used.

When no copolymer was formed, the molecular weight of the respective homopolymer was found to be lower than expected. Moreover, an increase of the acetal concentration in the feed gives rise to homopolymers having low molecular weights. The above features account for chain transfer processes between the growing chain radicals and the acetal. The chain transfer constant

of this monomer in the free radical polymerization of styrene was determined at 70°C by the conventional method²².

The number average molecular weight (\bar{M}_n) of polystyrene was determined by viscosimetric measurements in benzene at 25°C using the equation described in²³:

$$[\eta] = 11,3 \cdot (\bar{M}_n)^{0,73}$$

The value obtained for the chain transfer constant was:

$$C_t = 20,6 \times 10^{-4}$$

a) Copolymerization with acrylonitrile

When acrylonitrile is used, copolymer formation takes place under different experimental conditions. It has been reported also that acroleindibutylether acetals²⁵ can copolymerize with acrylonitrile. The polymerization rate

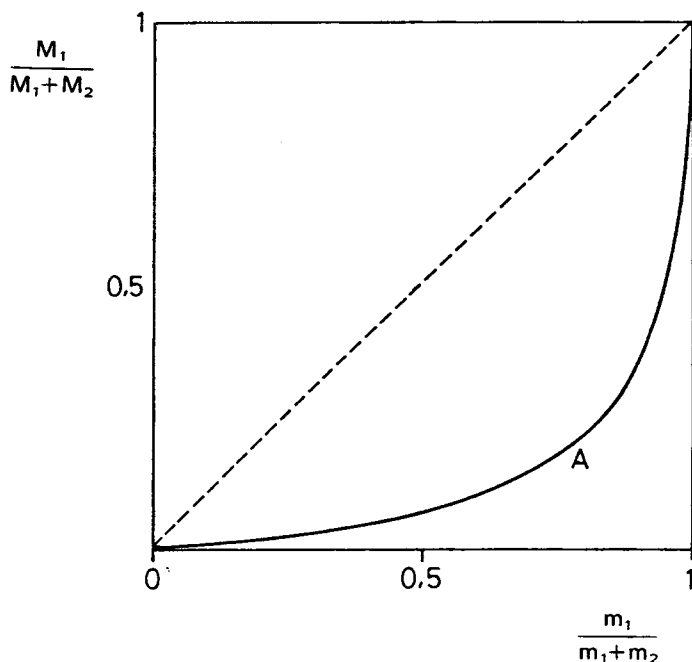


Fig. 3. Monomer-copolymer composition curve. M_1 : acroleindiethylacetal, M_2 : acrylonitrile.

appeared to decrease when the acetal concentration in the feed was increased. The monomer reactivity ratios were determined from the copolymer composition by the Fineman-Ross method²⁴. The obtained values in bulk are:

$$\begin{aligned}r_1 &= 0,02 \pm 0,00 \\ r_2 &= 11,19 \pm 0,50\end{aligned}$$

It is generally wellknown that allylic monomers have low polymerizability because of the degradative chain transfer. The monomer-copolymer composition curve is shown in Fig. 3.

The IR and NMR spectra of the copolymer showed the presence of carbonyl groups. The carbonyl group content in the copolymer increases proportional to the acetal mole fraction in the monomer feed. This indicates that the cleavage reaction of acetal groups, as shown in the reaction scheme, has taken place. For this reason the above reactivity ratio values must be taken into account with some caution.

b) Copolymerization with maleic anhydride

A copolymer between the acetal and maleic anhydride was readily obtained by free radical initiation of benzene solutions of the comonomers.

The copolymers exhibit remarkably uniform composition regardless of the monomer feed ratios. The experimental monomer reactivity ratio values were the following:

$$\begin{aligned}r_1 &= 0,18 \pm 0,04 \\ r_2 &= 0,07 \pm 0,01\end{aligned}$$

The remarkably uniform composition exhibited by the copolymers, regardless of monomer feed ratios, was suspected to account for a donor-acceptor complex between the two monomers. In order to prove the existence of a suspected association, a NMR study was carried out, using the equation given by Hanna and Ashbough²⁰ to determine the equilibrium constant of association or complexation. The value found was $8,5 \times 10^{-2} \text{ l} \cdot \text{mol}^{-1}$.

This result suggests that probably the complex species "homopolymerizes" which accounts for the degree of regularity in the copolymer composition.

- ¹ R. C. Schulz, H. Fauth, W. Kern, *Makromol. Chem.* **21** (1956) 227
- ² Y. Hachihama, *Kogyo Kagaku Zasshi* **62** (1959) 1924
- ³ R. C. Schulz, *Angew. Chem. Int. Ed. Engl.* **3** (1964) 416
- ⁴ J. H. Davies, P. Kirby, *Chem. Ind. (London)* (1964) 194
- ⁵ Ger. 707280 (1941), I. G. Farbenindustrie
- ⁶ U. S. 2467430 (1949), E. I. du Pont de Nemours and Co.
- ⁷ Brit. 679374 (1952), British Resin Co.
- ⁸ T. Ota, T. Otsu, M. Imoto, *Kogyo Kagaku Zasshi* **71** (1968) 736
- ⁹ J. L. Mateo, R. Sastre, *Rev. Plast. Mod.* **168** (1970) 454
- ¹⁰ J. L. Mateo, R. Sastre, *Makromol. Chem.* **157** (1972) 454
- ¹¹ J. L. Mateo, R. Sastre, *IUPAC Int. Symp. Macromol. (Helsinki) Prepr.* **2** (1972) 1-100
- ¹² J. L. Mateo, R. Sastre, *J. Polym. Sci. C* **42** (1973) 311
- ¹³ J. L. Mateo, R. Sastre, *IUPAC Int. Symp. Macromol. (Madrid) Prepr.* **1** (1974) 62
- ¹⁴ J. L. Mateo, R. Sastre, J. L. Acosta, *Rev. Plast. Mod.* **219** (1974) 850
- ¹⁵ R. Sastre, M. V. Dabrio, J. L. Mateo, *An. Quim.* **70** (1974) 905
- ¹⁶ H. Hibbert, M. S. Whelan, *J. Am. Chem. Soc.* **51** (1929) 3115
- ¹⁷ C. W. Smith, R. S. Fischer, *J. Org. Chem.* **25** (1960) 319
- ¹⁸ D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press (1966)
- ¹⁹ J. Fritz, N. M. Liski, *Anal. Chem.* **23** (1951) 589
- ²⁰ M. W. Hanna, A. L. Ashbaugh, *J. Phys. Chem.* **68** (1964) 811
- ²¹ J. H. Raley, F. F. Rust, W. E. Vaughan, *J. Am. Chem. Soc.* **70** (1948) 1336
- ²² F. R. Mayo, R. A. Gregg, M. S. Matherson, *J. Am. Chem. Soc.* **73** (1951) 1691
- ²³ D. H. Johnson, A. V. Tobolsky, *J. Am. Chem. Soc.* **74** (1952) 938
- ²⁴ M. Fineman, S. D. Ross, *J. Polym. Sci.* **5** (1950) 269
- ²⁵ N. Yashita, T. Seita, M. Toshihara, T. Maeshima, *J. Polym. Sci. B* **9** (1971) 641