

Thermal Stability of Nonionic Polyoxyalkylene Surfactants

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SYNOPSIS

Nonionic surfactants are largely employed in the pharmaceutical, cosmetic, and textile industry. The sensitivity of polyoxyethylene chains to autoxidation is studied because it is responsible for unpleasant effects such as discoloration, degradation of products, and unpleasant odors. In the present work, thermal stability of polyoxyethylene and polyoxyethylene/propylene nonionic surfactants has been studied by employing together differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). First of all, the thermal stability of three monodispersed surfactants (laurilic alcohol plus 4, 6, or 8 EO units) has been studied. Then, the behavior of these products has been compared with those of commercial surfactants containing the same alkyl chain coupled with hydrophilic chains of different lengths, containing EO units alone or both EO and PO. The effect of the alkyl chains has also been examined in the same way. In all cases, autoxidation starts at about 100°C with a net heat production proportional to the number of adducts and equal to about $(1.5\text{--}1.7) \times 10^5$ J/adduct. Heat evolution stopped at about the same temperature, independently of the hydrophilic chain length. A residual of 10–30% by weight decomposes, at higher temperatures, with a very small heat evolution. The interpretation of these and other phenomena observed conclude the paper.

INTRODUCTION

Nonionic surfactants, composed of saturated alkyl and polyoxyalkylene chains, are very sensitive to autoxidation.^{1,2} This reaction occurs with the demolition of the hydrophilic chain followed, as a consequence, by the loss of tensile properties.² Moreover, hydroperoxides and radicals formed in the autoxidation reaction are responsible for degradation and aging in several kinds of commercial products in which the mentioned surfactants are introduced as minor components, as, for example, in pharmaceutical and cosmetic preparations and in textiles. High temperatures strongly enhance autoxidation rates and, correspondingly, degradation effects. This fact is particularly important in the textile industry, because many fibers impregnated with surfactants are submitted to heat treatments. Therefore, for the industry, it is important to know the thermal stability at different temperatures of

nonionic surfactants in the presence of oxygen as well as the existing possibilities of inhibiting autoxidation. Different papers have been published about the autoxidation and degradation of polyoxyglycols,^{3–21} while fewer papers have been devoted to the autoxidation of nonionic surfactants.^{1,22–24} An exhaustive review on both such subjects has recently been published by Donbrow.² In this review, the stabilization of polyoxyalkylene derivatives has also been considered.²

The most employed methods reported in the literature for studying the autoxidation of polyoxyalkylene derivatives are the measurement of oxygen consumption, analysis of reaction products, especially hydroperoxides, and measurements of properties depending on the molecular weight (viscosity, cloud points, etc.).² The kinetic results obtained with the different techniques are controversial.

In the present work, thermal stability in the presence of air of polyethylene and/or polypropylene surfactants has been studied by employing two techniques, on the same sample: differential scanning calorimeter (DSC) and thermogravimetry

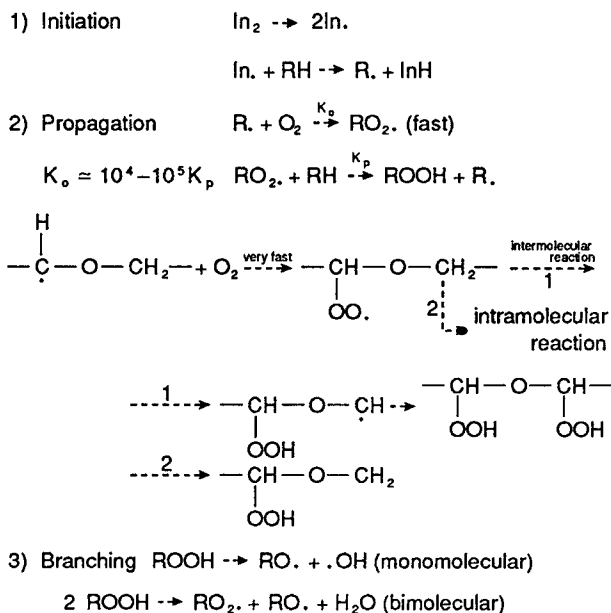
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(TGA). Runs have been performed by heating the samples at the same temperature scanning rate in both cases. Therefore, the evolution of weight loss and heat release, as a consequence of autoxidation, can be observed. The above-mentioned techniques have been employed, first of all, on three monodispersed samples of polyoxyethylene *n*-dodecanol, containing 4, 6, and 8 adducts, respectively. The same techniques have also been employed on commercial polyoxyethylene and polyoxyethylene/polyoxypropylene surfactants of different average molecular weight and on polyoxyglycols. The effect of some antioxidants have also been tested.

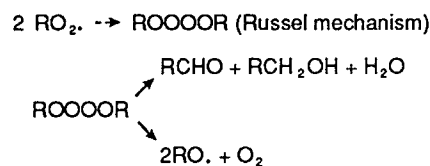
On the basis of the results achieved, some conclusions of general interest have been drawn in the interpretation of the behavior of nonionic surfactant autoxidation.

REACTION MECHANISM AND PRODUCTS

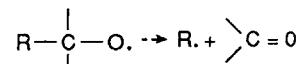
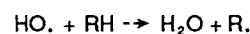
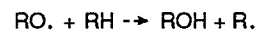
The mechanism of polyoxyethylene chain autoxidation is quite similar to that of hydrocarbon chains, but the presence of oxygen in the molecules strongly activates the process, which easily occurs also at room temperature.^{1,2} Hydrogen abstraction at carbon in the α position in respect to oxygen is the first reaction step. Then, molecular oxygen is quickly captured by the alkyl radical, giving a peroxy radical in the usual way. Hydroperoxides are formed by hydrogen abstraction via inter- or intramolecular paths. The reaction continues as in the following scheme^{1,2,25}:



4) Termination



5) Transfer



The last reaction of transfer, known as β -scission, is very important for the demolition of chains by autoxidation²⁵ and is strongly influenced by high temperature and solvent polarity.

Acidity plays a catalytic role both in the formation and decomposition of hydroperoxides.² The reaction is, therefore, autocatalytic because hydroperoxides are themselves acidic and form acetic and formic acids as reaction products. Many other reaction products can be formed, and many have been recognized, as, for example, formaldehyde, glycols and their aldehydes, hemiformals and formates, and water and CO_2 .² Generally, a random scission of the chains has been assumed^{9,26} to occur more probably than does a stepwise degradation.

EXPERIMENTAL

Stability runs have been performed by employing a differential scanning calorimeter (Model 910) and a thermogravimeter (Model 952) of DuPont Instruments Co., both connected with the data analyzer (Model 1090). Runs were performed in both cases by putting a small sample of the surfactant (3–10 mg) in a suitable cup, closing the apparatus, and flushing with a constant 60 cm^3/min flux of air. Then, the temperature of the sample was increased at the constant rate of 5°C/min and weight loss or heat evolution were registered as a function of temperature.

Stability runs were performed on monodisperse polyoxyethylene *n*-dodecanol with 4, 6, and 8 adducts, respectively, supplied as pure compounds by Nikko Chemicals Co. Other stability runs were performed on commercial samples of nonionic surfactants provided by Lamberti SpA.

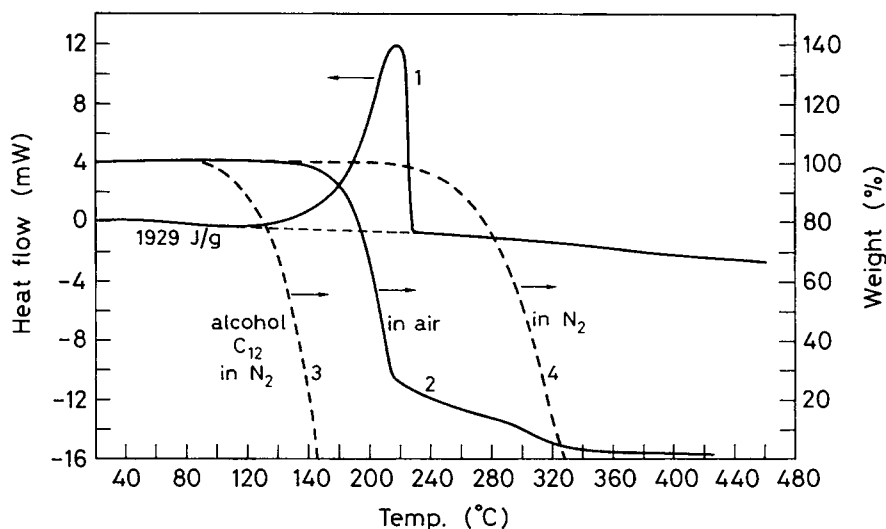


Figure 1 Oxidative thermal degradation of monodispersed polyoxyethylene (4 adducts) *n*-dodecanol; DSC (curve 1), TGA (curve 2). Dotted lines correspond to vaporization in nitrogen of *n*-dodecanol (curve 3) and of the mentioned surfactant (curve 4).

RESULTS AND DISCUSSION

First of all, the oxidative thermal degradation of polyoxyethylene *n*-dodecanol with a defined number of adducts has been studied. In Figures 1–3, DSC and TGA curves are reported in the same plot; these curves have been obtained for polyoxyethylene *n*-dodecanol with 4, 6, and 8 adducts, respectively. The two dotted lines in the same figures correspond to the weight loss of *n*-dodecanol and of the examined

surfactant, respectively, for vaporization in a nitrogen stream. As can be seen, in any case, heat starts developing at about 110°C and ceases at about 240°C, independently of the hydrophilic chain length. Heat evolution occurs quite contemporarily with the 85% loss of weight. No increase in the samples' weight is observed, that is, formation and decomposition of peroxides have the same rates and the weight balance is null. The residual, about 15% by weight, decomposes at a slower rate and at higher

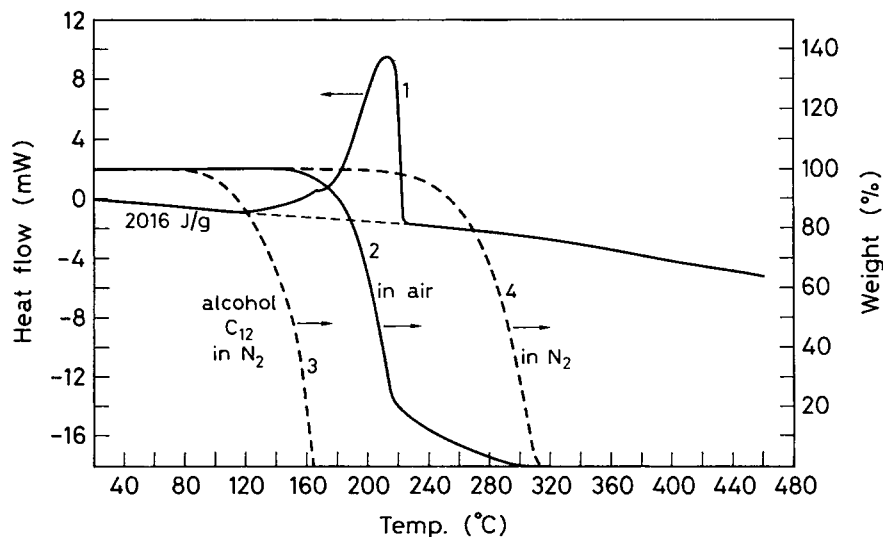


Figure 2 Oxidative thermal degradation of monodispersed polyoxyethylene (6 adducts) *n*-dodecanol; DSC (curve 1), TGA (curve 2). Dotted lines correspond to vaporization in nitrogen of *n*-dodecanol (curve 3) and of the mentioned surfactant (curve 4).

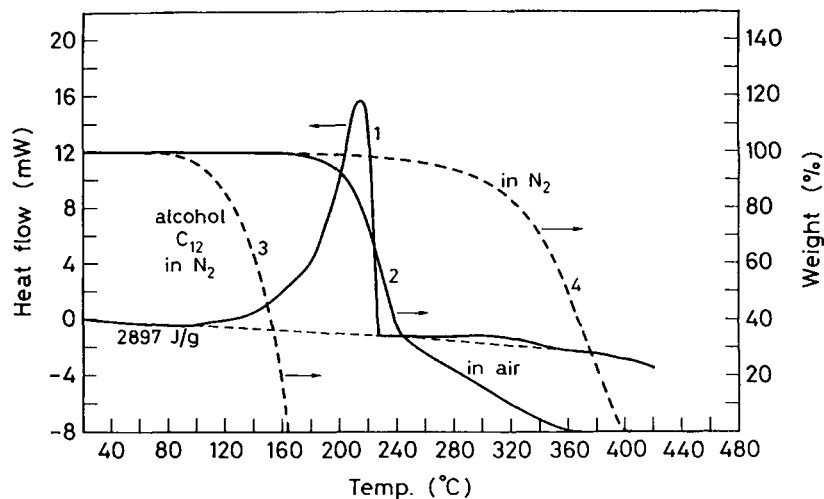


Figure 3 Oxidative thermal degradation of monodispersed polyoxyethylene (8 adducts) *n*-dodecanol; DSC (curve 1), TGA (curve 2). Dotted lines correspond to vaporization in nitrogen of *n*-dodecanol (curve 3) and of the mentioned surfactant (curve 4).

temperature. This fact suggests the intervention of an oxidative pyrolysis of higher molecular weight molecules, formed as a consequence of radical termination, probably between alkyl radicals.

By comparing the thermogravimetric curves obtained with those of the nitrogen stream, for *n*-dodecanol and the corresponding surfactant, it can be shown that in all three mentioned cases 85% of the weight loss corresponds to the evaporation of a surfactant containing about two adducts, independently of the hydrophylic chain length.

This fact, together with the above-mentioned observation that heat evolution occurs in the same temperature range of 110–240°C, suggests that the larger the hydrophylic chain is, the faster is the demolition reaction, in agreement with previous observations reported in the literature related to polyoxyethylene chains.²⁶

The findings described are confirmed by the behavior of a commercial surfactant of polyoxyethylene *n*-dodecanol with average molecular weight 900 (see Fig. 4). In this case, in fact, heat evolution oc-

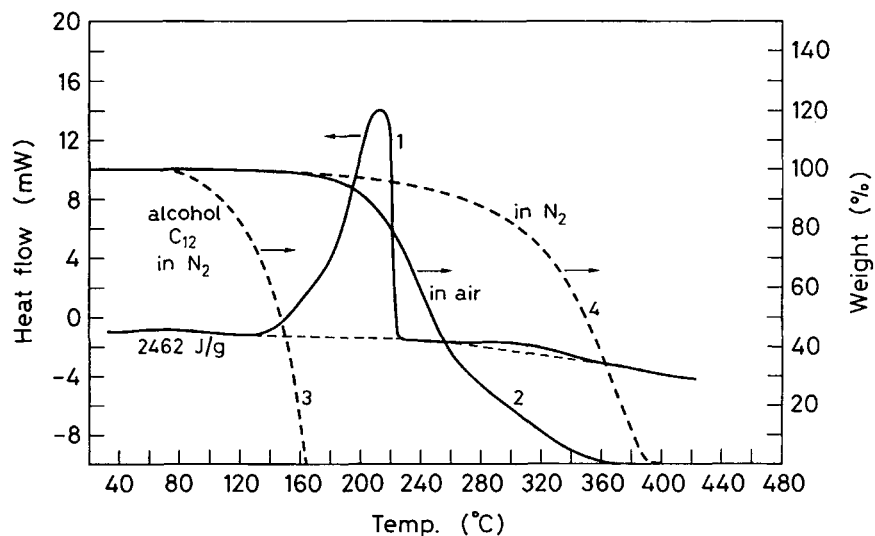


Figure 4 Oxidative thermal degradation of polyoxyethylene *n*-dodecanol with average MW = 900; DSC (curve 1), TGA (curve 2). Dotted lines correspond to vaporization in nitrogen of *n*-dodecanol (curve 3) and of the mentioned surfactant (curve 4).

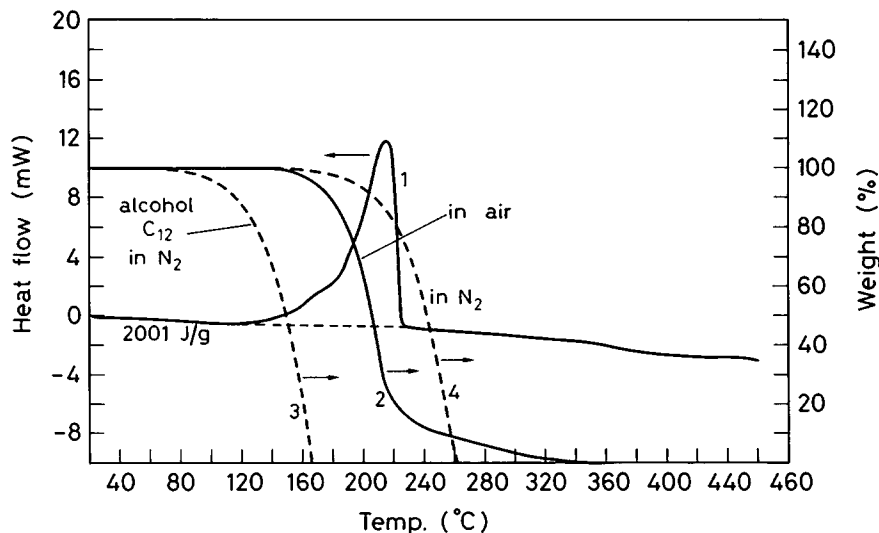


Figure 5 Oxidative thermal degradation of polyoxyethylene/propylene *n*-dodecanol with average MW = 957; DSC (curve 1), TGA (curve 2). Dotted lines correspond to vaporization, in nitrogen lives of the mentioned surfactant (curve 4).

curs also in the same temperature range, while the first part of the weight loss curve is only moderately shifted to higher temperatures. Residuals, decomposing more slowly, are now about 30%. The presence of propyleneoxide units in the hydrophilic chains does not remarkably affect the stability and behavior of a polyoxyethylene/polyoxypropylene *n*-dodecanol of molecular weight 957 (5 EO + 9.5 PO), similar to that shown in Figure 4 and which can be seen in Figure 5.

In Figures 6 and 7, we can see the behavior of polyoxyethylene/polyoxypropylene of C_{12} - C_{18} fatty alcohols with different average molecular weights of 900 and 1840, respectively. Again, it is confirmed that the longer the hydrophilic chain is, the faster is the demolition reaction. Moreover, it can also be shown that the longer the hydrophilic chain is, the higher is the heat developed.

Figures 8 and 9 show the DSC and TG curves obtained with polyoxyethylene/propylene copoly-

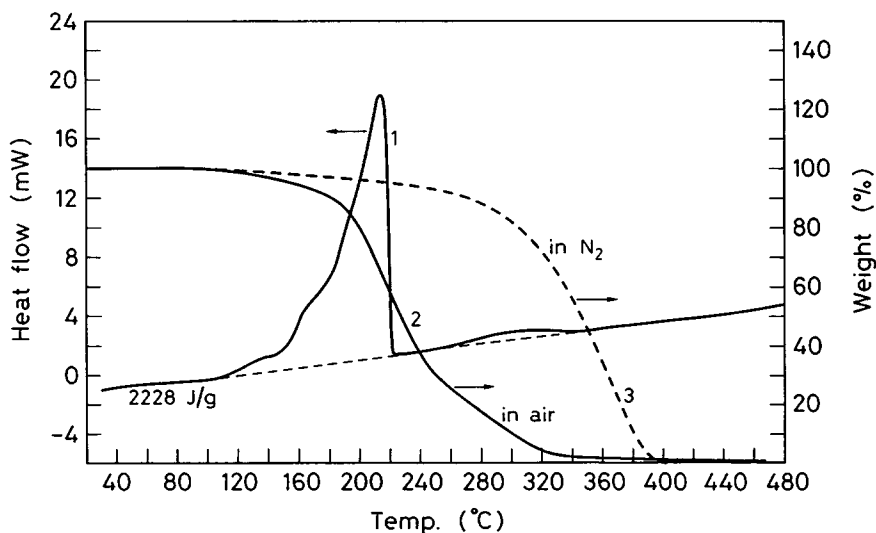


Figure 6 Oxidative thermal degradation of polyoxyethylene/propylene fatty alcohol C_{12} - C_{18} with average MW = 900; DSC (curve 1), TGA (curve 2). Dotted line (curve 3) corresponds to the vaporization in nitrogen of the mentioned surfactant.

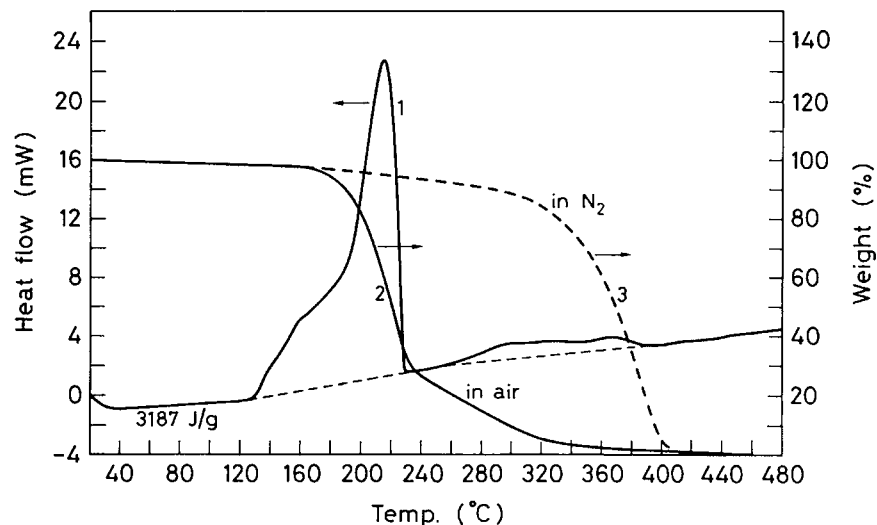


Figure 7 Oxidative thermal degradation of polyoxyethylene/propylene fatty alcohol C_{12} - C_{18} with average MW = 1840; DSC (curve 1), TGA (curve 2). The dotted line (curve 3) corresponds to the vaporization in nitrogen of the mentioned surfactant.

mers of different molecular weight, i.e., 1050 and 2900, respectively. The kinetic behavior of these copolymers is the same observed for the surfactants, except for the slow rate decomposition of the residual. As can be seen, in this case, the phenomenon has nearly disappeared. This fact suggests that the slow decomposition at high temperatures is mainly due to the addition of the hydrophobic chains by radical termination.

From all the runs considered, it is possible to observe that the heat balance is largely positive, though the oxidative degradation occurs together with the vaporization of the decomposition products. If we put the net heat released from EO surfactants as a function of the molecular weight or the number of adducts, a linear trend is obtained, as it appears in Figure 10. The same figure also reports the heat released per each adduct as a function of the number

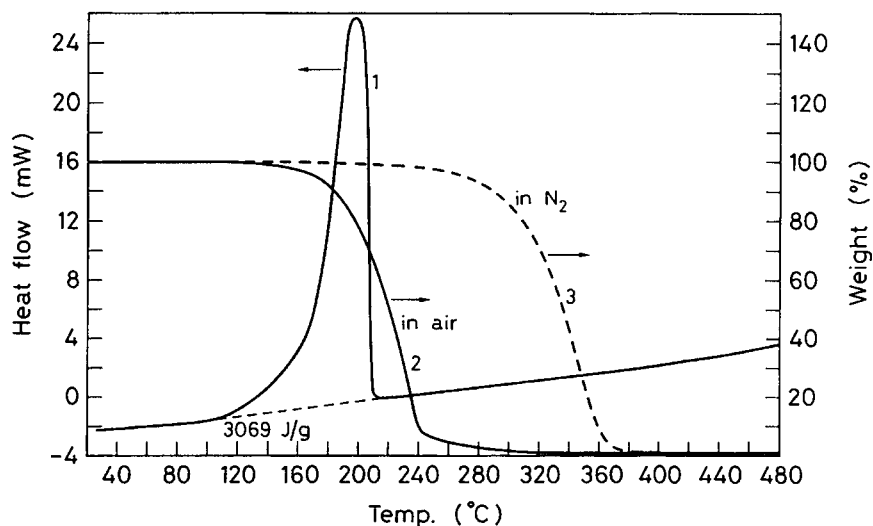


Figure 8 Oxidative thermal degradation of EO/PO copolymers, of average MW = 1050; DSC (curve 1), TGA (curve 2). The dotted line (curve 3) corresponds to vaporization in nitrogen.

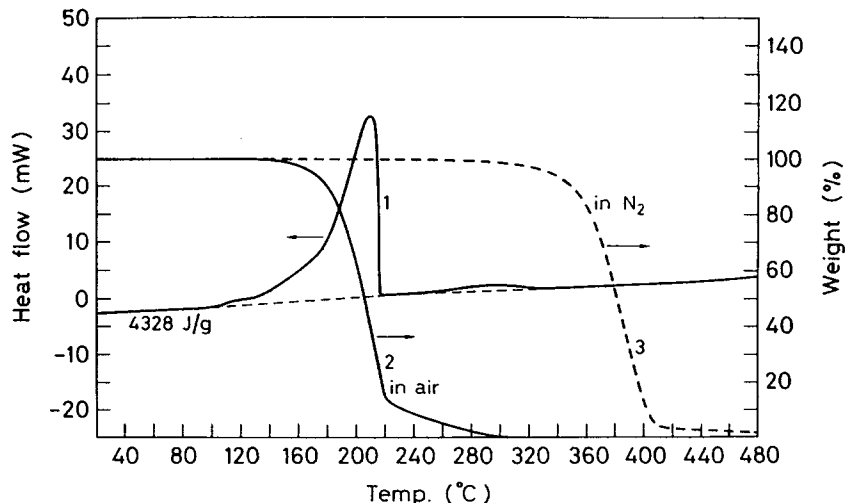


Figure 9 Oxidative thermal degradation of EO/PO copolymers of average MW = 2900; DSC (curve 1), TGA (curve 2). The dotted line (curve 3) corresponds to vaporization in nitrogen.

of adducts. As can be seen, a constant value of about 150,000 J/adduct is obtained. A similar diagram has also been drawn for EO/PO surfactants, including also EO/PO copolymers. Again, a linear trend is obtained for the net heat released as a function of the number of adducts and a constant value of about 178,000 J/adduct is also obtained.

In this case, each adduct has been considered as having a mean value of molecular weight between ethylene and propylene oxide. The plots reported in

Figures 10 and 11 confirm that the hydrophobic part of the surfactant is poorly involved in oxidative degradation. Therefore, hydrophobic chains have great probabilities of coupling by termination because of the long reaction time.

A small amount of heat is then developed at high temperatures, in correspondence to the residual decomposition (see Figs. 4-6). The fact clearly indicates that pyrolysis is prevailing instead of oxidation.

The formation of a poorly autoxidable residual has also been confirmed through isothermal runs.

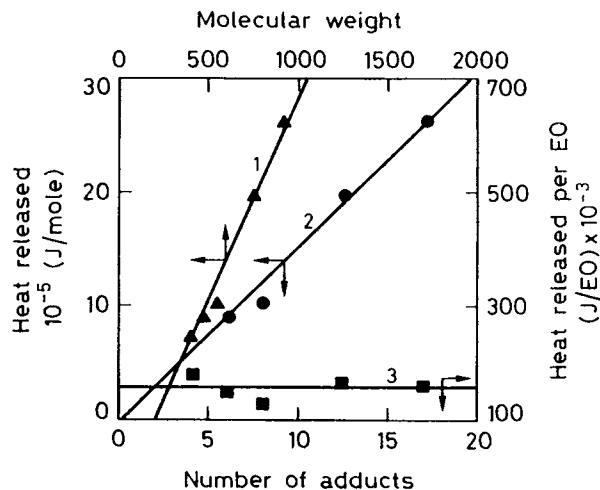


Figure 10 Net heat released from EO surfactants as a function of molecular weight (curve 1) and number of adducts (curve 2), respectively. In the same plot, the heat released per EO unit is also reported as function of EO units (curve 3).

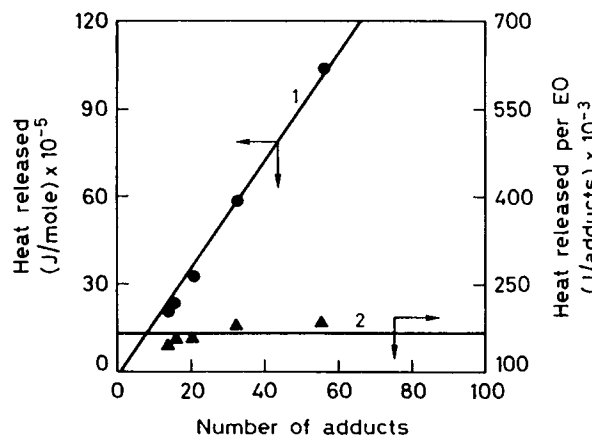


Figure 11 Net heat released from EO/PO surfactants as a function of the number of adducts (curve 1). In the same plot, the specific heat release is also reported in relation to the adduct unit. In this case, the adduct considered is the mean molecular weight between ethylene and propylene oxide.

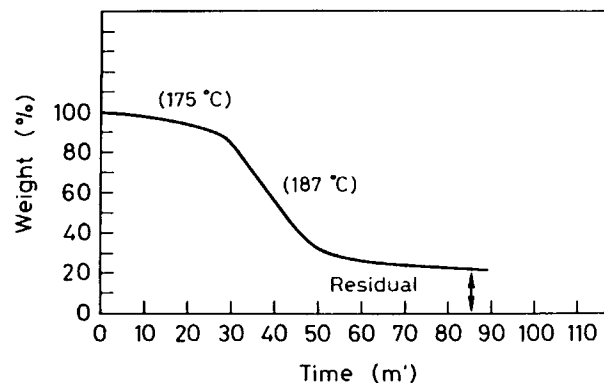


Figure 12 Oxidative thermal degradation of a polyoxyethylene/propylene of fatty alcohol C_{12} - C_{18} with average MW = 900 observed at TGA under two different isothermal conditions.

Figure 12 shows, as an example, two of these isotherms. From this figure, it can be observed that reaction rates are very sensitive to temperature and that a poorly autoxidizable residual of about 20% is also formed under these conditions. An antioxidant could hinder autoxidation. However, it is known from the literature¹⁶ that only phenothiazine is effective even at elevated temperatures ($> 150^{\circ}\text{C}$).

Figure 13 reports the behavior of a commercial surfactant polyoxyethylene/propylene of fatty alcohol (C_{12} - C_{15}) of MW = 900 containing 0.2% of phenothiazine. As can be seen, the reaction starts at temperatures higher than normal but with an explosive reaction rate.

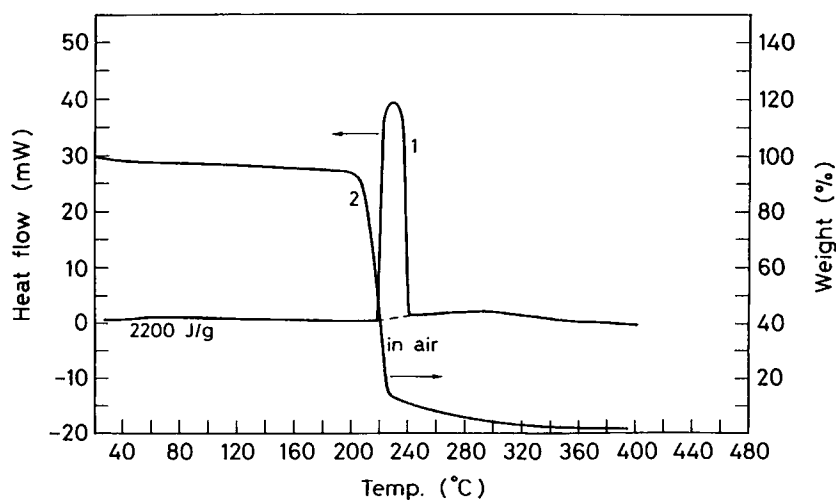


Figure 13 Effect of 0.2% of phenothiazine in the oxidative thermal degradation of a polyoxyethylene/propylene of fatty alcohol C_{12} - C_{18} with an average MW = 900. Curve 1 refers to the DSC, and curve 2, to TGA.

Reaction starts at 218.5°C and terminates at 240°C . Besides, it is very interesting to observe that the reaction is almost complete, the residual being almost less than 10%. This is caused by an autoxidation characterized by a small number of radicals and a very fast reaction with long radical chains.

CONCLUSIONS

The autoxidation of nonionic surfactants containing oligomers of ethylene oxide and/or propylene oxide, in the hydrophilic chains, occurs when temperature is gradually increased by following two kinetic patterns. The first of them is characterized by the hydrophilic chain demolition and the second by the slow oxidative pyrolysis of molecules formed by addition of the residual hydrophobic chains, as a consequence of radical termination reactions.

The oxidative demolition of the hydrophilic chains is a strongly exothermic process developing about 150,000–170,000 J for each mole of adduct. The longer the hydrophylic chain is, the faster is the reaction of demolition. This kinetic behavior is similar to that observed for the autoxidation of ethylene oxide polymers and EO/PO copolymers. This observation has already been reported in the literature^{16,26} and the behavior has been attributed to an increase in the resistance to autoxidation as a consequence of the increasing hydroxyl concentration in the reaction system.

Thus, we also think it is important how chain

demolition occurs. In fact, we could hardly justify this behavior if the rupture of the hydrophylic chains occurs step-by-step from the end of the molecules, while this can more easily be justified by considering a rupture statistically occurring in the middle of the chain, together with the autocatalytic formation and decomposition of hydroperoxides.

As has been observed, autoxidation is very sensitive to temperature and an apparent activation energy of about 48 kcal/mol can be estimated from the isothermal run of Figure 12. This very high value of apparent activation energy can be explained as a consequence of autocatalysis in the hydroperoxide formation and decomposition, following the increase in acidity of the medium. By increasing temperature, the β -cleavage mechanism becomes competitive in respect to the Russell one and chain demolition is more and more favored.

In the presence of antioxidants, the reaction starts at higher temperatures but with explosive reaction rates and producing small amounts of residual. In this case, the formation of hydroperoxides is hindered until the antioxidant is destroyed. But this occurs only when the temperature is very high and, correspondingly, the reaction is very fast. β -Scission predominates in this case, and the hydrophylic chains are quickly destroyed. In this situation, the probability of alkyl radical termination is small and high molecular weight residuals are therefore formed in small amounts.

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REFERENCES

1. R. Hamburger, E. Azaz, and M. Donbrow; *Pharm. Acta Helv.*, **50**(1/2), 10 (1975).
2. M. Donbrow, *Stability of the Polyoxyethylene Chain in Nonionic Surfactants*, Vol. 23, M. J. Schick, Ed., Marcel Dekker, New York, 1987.
3. W. G. Lloyd, *J. Am. Chem. Soc.*, **78**, 72 (1956).
4. C. Decker and J. Marchal, *Makromol. Chem.*, **166**, 117 (1973).
5. C. Decker and J. Marchal, *Makromol. Chem.*, **166**, 139 (1973).
6. P. Grosborne, I. Sereé de Roch, and L. Sajus, *Bull. Soc. Chim.*, 2020 (1968).
7. W. G. Lloyd, *J. Polym. Sci. A*, **1**, 2551 (1963).
8. C. Decker and J. Marchal, *Makromol. Chem.*, **166**, 155 (1973).
9. C. Crouzet and J. Marchal, *Makromol. Chem.*, **166**, 69 (1973).
10. C. Decker and J. Marchal, *Makromol. Chem.*, **175**, 3531 (1974).
11. C. Decker and J. Marchal, *Makromol. Chem.*, **15**, 799 (1977).
12. L. Dulong and G. Storck, *Makromol. Chem.*, **91**, 50 (1966).
13. M. Donbrow, R. Hamburger, E. Azaz, and A. Pillersdorf, *Analyst*, **103**, 400 (1978).
14. L. Chafetz, W. Hong, D. C. Tsiliforus, A. K. Taylor, and J. Philip, *J. Pharm. Sci.*, **73**, 1186 (1984).
15. C. Crouzet and J. Marchal, *Makromol. Chem.*, **166**, 99 (1973).
16. W. G. Lloyd, *J. Chem. Eng. Data*, **6**, 541 (1961).
17. C. Decker, *J. Polym. Sci. Polym. Chem. Ed.*, **15**, 781 (1977).
18. C. Crouzet and J. Marchal, *Makromol. Chem.*, **166**, 85 (1973).
19. C. Hassal, *Organic Reactions*, Vol. 9, Wiley-Interscience, New York, 1970, p. 141.
20. G. A. Russel, *J. Am. Chem. Soc.*, **79**, 3871 (1957).
21. C. W. McGary, *J. Polym. Sci.*, **46**, 51 (1960).
22. A. M. Afifi-Effat and J. N. Hay, *Eur. Polym. J.*, **8**, 289 (1972).
23. M. Donbrow and E. Azaz, *J. Coll. Interface Sci.*, **57**, 20 (1976).
24. M. Donbrow, R. Hamburger, and E. Azaz, *J. Pharm. Pharmacol.*, **27**, 160 (1975).
25. E. Santacesaria and N. Pimpinelli, *Chim. Ind.*, **68**(7/8), 69 (1986).
26. P. Grosborne and I. Sereé de Roch, *Bull. Soc. Chim.*, 2260 (1967).

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