Stabilisation of Polyethylene Cross-linked in the Presence of Peroxides. Study of Chemical Changes Taking Place in the DCP – Irganox 1081 System at Low Temperatures

S. Kudła, J. Poskrobko

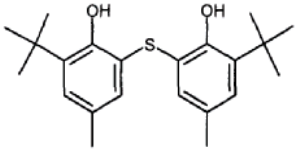
Institute of Heavy Organic Synthesis, Kędzierzyn-Koźle, Poland

Abstract

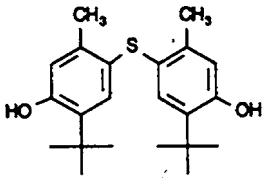
Chemical cross-linking of polyethylene is widely used for polymer properties modification. As cross-linking agents organic peroxides, mainly dicumyl peroxide (DCP), are applied. For improvement of thermooxidative stability addition of stabilisers is necessary. Among them sulphur containing hindered phenols are well known [1], such as commercially available Irganox 1081, Irganox 1035 or Lowinox TBM 6. In our team we have investigated [2-4] the stabilisation processes taking place during cross-linking of LDPE in the presence of dicumyl peroxide and 6,6`-di-tert-butyl-2,2`-thiodi-p-cresol (Irganox 1081). In this paper we described results of our experimental works concerning the interaction of DCP with Irganox 1081 in air atmosphere, at temperatures below fast peroxide decomposition.

It is well known, that 6,6`-di-tert-butyl-2,2`-thiodi-p-cresol (Irganox 1081) undergoes oxidation during compounding which causes appearance of colour (yellowish to reddish) [5]. This colour disappears in time because it is not stable towards diffuse light. Following compounds are responsible for this effects: benzoquinone (visible absorption λ_{max} = 443 nm), diphenoquinone (423 nm), and stilbenequinone (452 nm). There was also supposition, that Irganox 1081 during oxidation forms high molecular (oligomers) products.

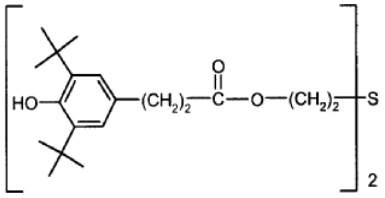
During our experiments performed with Irganox 1081 alone we found out, that heating up to 110°C do not cause the appearance of colour, even in air atmosphere. After adding dicumyl peroxide the situation was quite different. At low (0,3-3) molar ratio DCP/Irganox 1081 in air atmosphere, and at all of ratios investigated under nitrogen, the products have been coloured yellow. At higher (3-10) molar ratios DCP/Irganox 1081, products of their reactions at 110°C in air atmosphere were intensively red. This effect is not visible when others sulphur containing hindered phenols, like Lowinox TBM 6 or Irganox 1035, are used.



Irganox 1081



Lowinox TBM 6



Irganox 1035

The aim of our work was to examine reactions undergoing during heating DCP with Irganox 1081, at different molar ratios, in the air atmosphere, at 110°C. At this relatively low temperature the fast, radical decomposition of DCP does not take place yet [6].

In the first phase of our experiments we have measured the absorbance, at 480 nm, of xylene solutions of reaction products obtained during heating at 110°C mixtures of DCP and Irganox 1081 at various molar ratios. The results are presented in Fig.1. The shape of this curve is quite surprising.

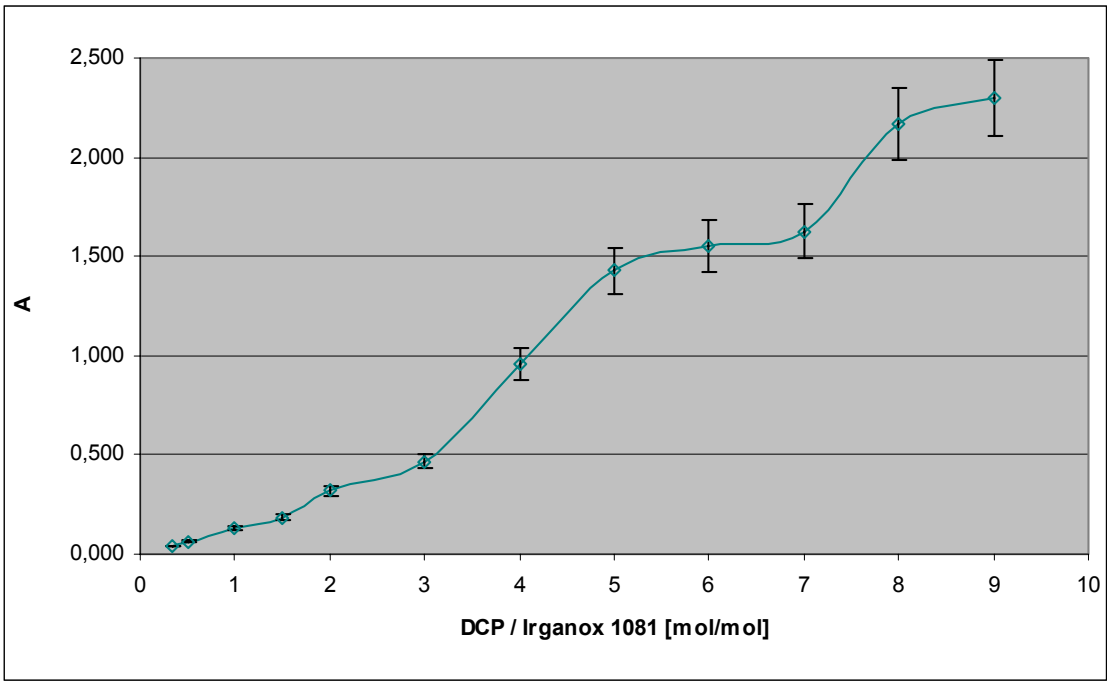


Figure 1. Absorbance at 480 nm for xylene solutions of DCP/Irganox 1081 mixtures heated for 30 min. at 110°C in the air atmosphere.

To understand better the chemical processes taking place between this two compounds, chromatographic analysis was performed. Figure 2 shows the GPC analysis result, with detection at 480 nm. As it can be seen, beside peaks attributed to DCP and Irganox 1081, there appeared three additional peaks, which intensities depend on DCP/Irganox 1081 molar ratios. The tentative molar masses of this products are: 930, 1400, and 1840.

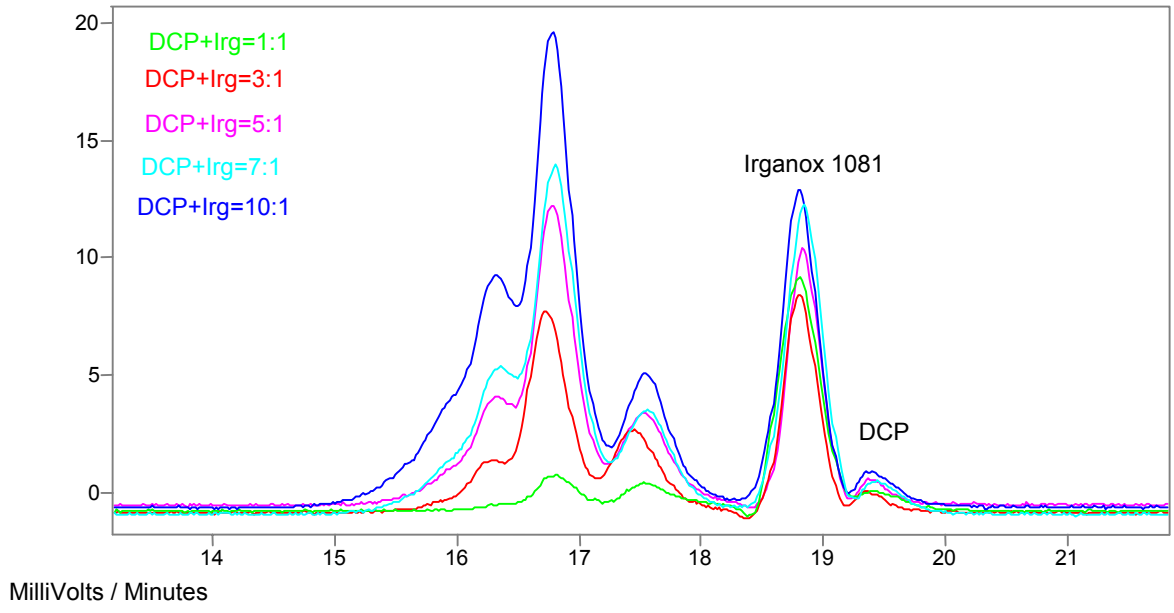


Figure 2. GPC results for reactions products of DCP with Irganox 1081 at molar ratios from 1:1 to 10:1 (detection at 480 nm).

Analysis performed for product with the highest investigated molar ratio (10:1) were repeated after 96 hours (Figure 3). The intensities of additional peaks are visibly weaker; the colour of the solution indeed turned pale. However, analogical GPC analysis, but performed with refractometric detector revealed that the intensities of aforementioned additional peaks, measured 5 hours after dissolution of reaction product in xylene, and after 192 hours, are practically the same (Figure 4).

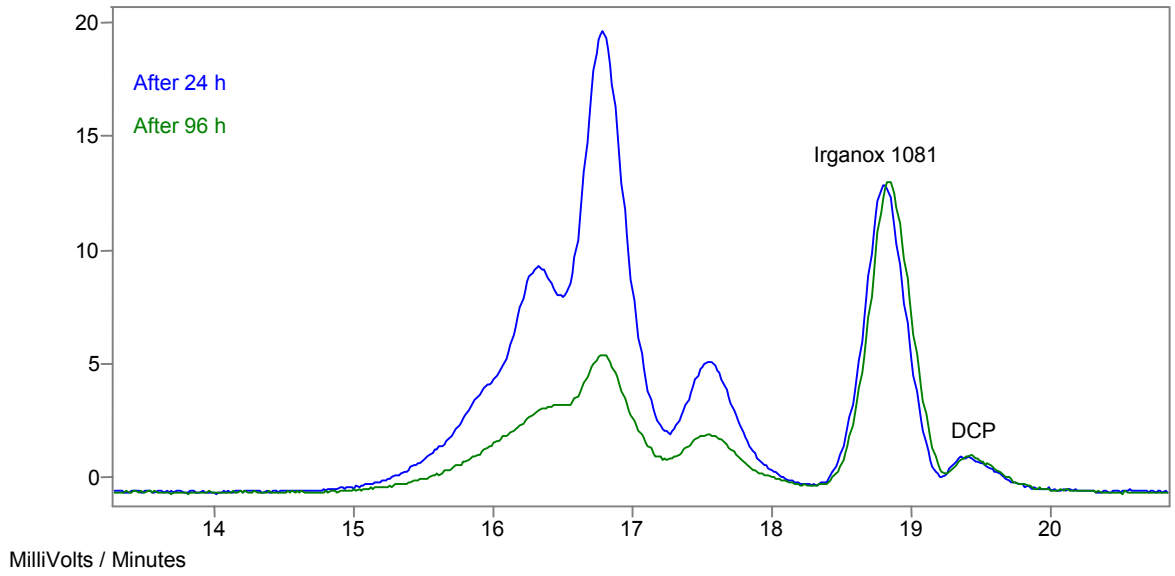


Figure 3. GPC analysis results for reaction product of DCP and Irganox 1081 (10:1 molar ratio) obtained after 24 hours (upper curve) and after 96 hours after dissolution (detection at 480 nm).

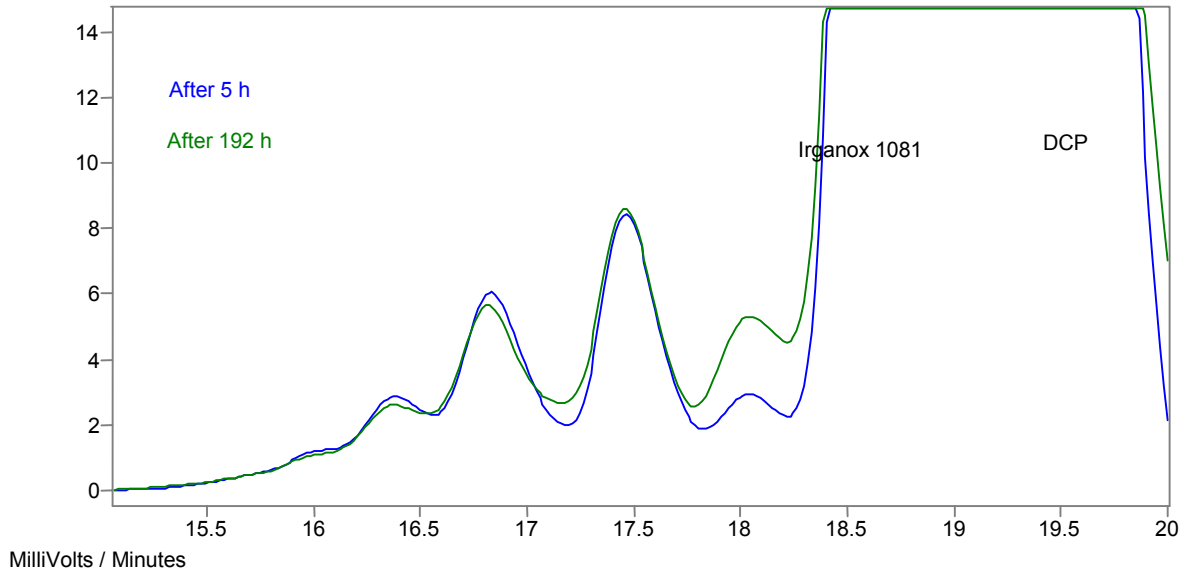


Figure 4. GPC analysis results for reaction product of DCP and Irganox 1081 (10:1 molar ratio) obtained after 5 hours and after 96 hours after dissolution (refractometric detection).

In order to closely characterize this products, we have made FTIR analysis of DCP and Irganox 1081 mixtures heated up to 60° and up to 110°C. As a result we stated that the only difference is appearing of the peak at 1700-1680 cm^{-1}, characteristic for carbonyl groups, after heating to 110°C.

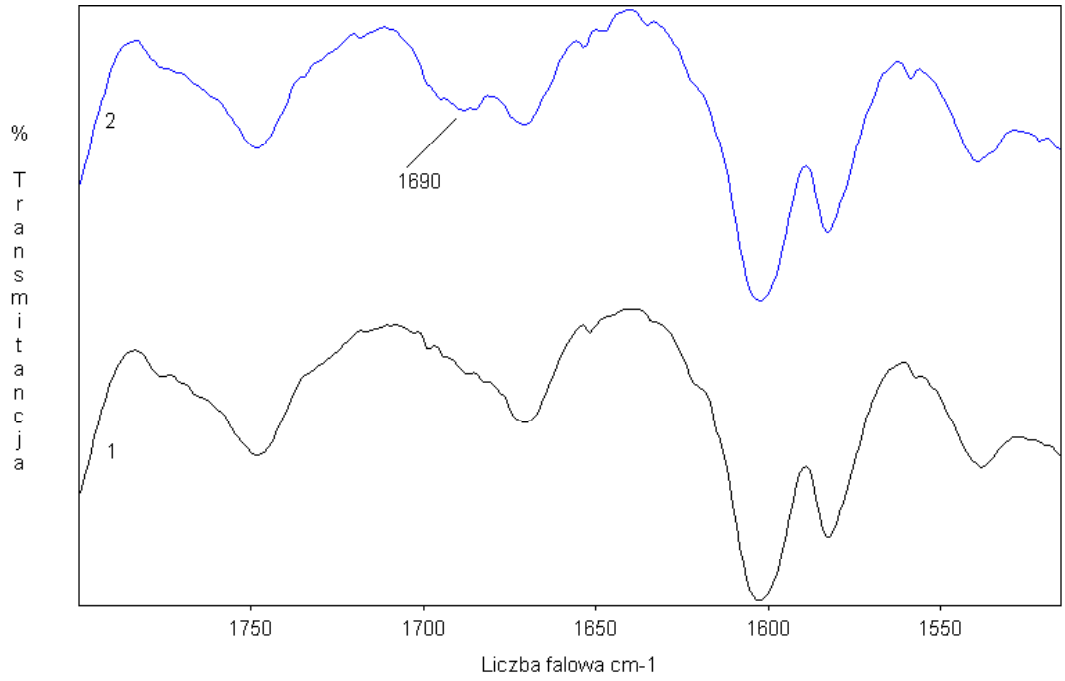


Figure 5. FTIR analysis results of mixtures of DCP and Irganox 1081 (10:1 mol ratio), heated up to 60°C (spectrum 1) and 110°C (spectrum 2).

Conclusions

According to our results the oxidation of Irganox 1081 at 110°C has a complex character and leads to different products depending on reaction conditions. A key issue in this process is the presence and amount of used peroxide. In the absence of DCP the air oxidation of Irganox 1081 does not lead to coloured products. At different DCP/Irganox 1081 molar ratios at least three products are formed, which can additionally undergo intramolecular rearrangements.

References

1. G. Scott, *Peroxidolytic Antioxidants: Sulphur Antioxidants and Autosynergistic Stabilisers based on Alkyl and Aryl Sulphides* in *Developments in Polymer Stabilisation-6*, pp. 29-71, Applied Science Publishers, (1983)
2. M. Uhniat, S. Kudła, *Stabilisation of LDPE Cross-Linked in the Presence of Peroxides I. Kinetic Study of the Oxidation*, Polym. Degrad. Stab. **71**, pp. 69-74 (2001)
3. M. Uhniat, M. Sudoł, S. Kudła, *Stabilisation of LDPE Cross-Linked in the Presence of Peroxides II. FTIR Study of Chemical Changes Taking Place in the LDPE-Dicumyl Peroxide-Irganox 1081 System*, Polym. Degrad. Stab. **71**, pp. 77-82 (2001)
4. M. Uhniat, S. Kudła, E. Dziwiński, M. Sudoł, *Stabilisation of LDPE Cross-Linked in the Presence of Peroxides III. Mass Spectrometric Study of Chemical Changes Taking Place in the n-octadecene-Dicumyl Peroxide-Irganox 1081 System*, Polym. Degrad. Stab. **71**, pp. 83-91 (2001)
5. Ciba Specialty Chemicals information brochure
6. T. Yamazaki, T. Seguchi, *ESR Study on Chemical Crosslinking Reaction Mechanisms of Polyethylene Using Chemical Agent*, J. Polym. Sci.: part A: Polym. Chem. **35**, 279-284 (1997)