

ANTIOXIDANTS AND STABILIZERS—LXVIII*. REACTIONS OF HYDROPEROXIDES MODELLING OXIDIZED POLYOLEFINS WITH 2,6-DITERTBUTYL- 4-METHYLPHENOL†

J. KOVÁŘOVÁ-LERCHOVÁ and J. POSPÍŠIL

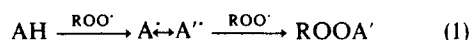
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6,
Czechoslovakia

(Received 23 March 1977)

Abstract—Hydroperoxides modelling oxidized segments of the polyolefin chain were synthesized. Reaction of derived alkyl-peroxyls with 2,6-ditert-butyl-4-methylphenol, under the conditions of inhibited oxidation, yielded 4-alkyl-peroxy-2,5-cyclohexadienones which were characterized. These compounds accelerate the thermal oxidation of tetralin. The investigation confirmed the main mechanism of transformation of the phenolic antioxidant due to the alkylperoxy radicals arising by autoxidation of hydrocarbon substrates.

INTRODUCTION

The stabilization of polyolefins with phenolic antioxidants is still a process of prime importance. This type of antioxidant undergoes chemical changes because of reactions during the stabilization process [1]. One of the most important steps leading to transformation is formation of an aryloxy radical A' from the phenolic antioxidant AH after interaction with the alkylperoxyl ROO' formed from the hydrocarbon substrate. The aryloxy radical undergoes further transformations in keeping with its reactivity. We investigated in detail one of these reactions, in which mesomerization of the aryloxy radical A' into A'' is followed by interaction of A'' with another ROO' . The reaction results in the formation of isomeric alkylperoxy cyclohexadienones $ROOA'$.

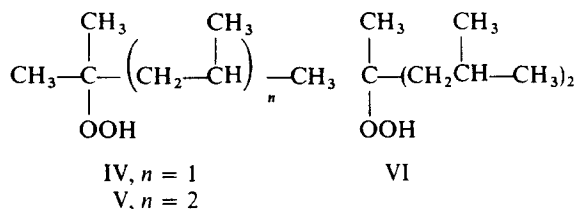
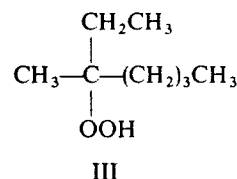
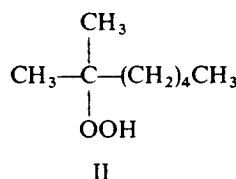
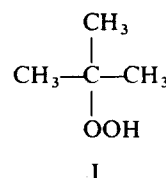


Transformations of mono-, [2] bi- [3] and tri-nuclear [4,5] phenolic antioxidants were studied under conditions modelling the inhibited oxidation of polyolefins during ageing, connected with transformation of the original antioxidant into derivatives of 4-alkylperoxy-2,5-cyclohexadienone ($ROOA'$). In all cases *tert*-butylhydroperoxide (I) was used, being the simplest low-molecular weight model for polypropylene hydroperoxide. We isolated and identified reaction products and investigated the properties of the $ROOA'$ -type compounds formed in the reaction.

In this work the phenolic component was represented by a typical mononuclear antioxidant, 2,6-ditert-butyl-4-methylphenol; alkylperoxyls were generated from hydroperoxides II–VI derived from branched hydrocarbons containing 5–7 carbon atoms in the chain.

* Part LXVII. *Angew. Makromol. Chem.* in press.

† Presented on 9th Conference of the Danubian states "Natural and artificial aging of plastics", Gottwaldov, 20–24 September 1976.



EXPERIMENTAL

Chemicals and model compounds

Ketones for syntheses of hydroperoxides were purified by fractional distillation (b.p.°O/kPa): methyl isobutyl ketone (115/99.99), 4,6-dimethyl-2-heptanone (108/13.46), diisobutyl ketone (102/13.33).

2-methyl-2-heptanol (b.p. 168°) and 3-methyl-3-heptanol (b.p. 162°) were redistilled products of Koch Light Lab. Ltd. Further alcohols were prepared by reacting ketones with a molar amount of freshly prepared methylmagnesium iodide. The products were redistilled before use; purities were checked by gas chromatography (b.p.°C/kPa): 2,4-dimethyl-2-pentanol (60.5/5.33), 2,4,6-trimethyl-2-heptanol (87/3.33), 2,4,6-trimethyl-4-heptanol (65/1.46).

The hydroperoxides were prepared by a modified procedure after Davies [6], by oxidation of alcohols with 80% hydrogen peroxide at 0–5° and molar ratio alcohol/H₂O₂ 1:8. Products were isolated and repeatedly distilled at

Table 1. Characteristics of alkylhydroperoxides II-VI

| Compound | B.p. °C/Pa | n_D^{20} | ROOH content, % Iodometrically | i.r. |
|--|---------------|------------|-----------------------------------|------|
| 2-Methyl-2-hydroperoxyheptane(II) | 48/266.6 | 1.4291 | 89.48 | 89.1 |
| 3-Methyl-3-hydroperoxyheptane(III) | 45/266.6 | 1.4330 | 92.52 | 91.2 |
| 2,4-Dimethyl-2-hydroperoxypentane(IV) | 48/399.9 | 1.4265 | 98.71 | 92.5 |
| 2,4,6-Trimethyl-2-hydroperoxyheptane(V) | 62/266.6 | 1.4375 | 94.17 | 91.4 |
| 2,4,6-Trimethyl-4-hydroperoxyheptane(VI) | 65/266.6 | 1.4404 | 95.44 | 91.6 |

reduced pressure. Impurities due to the starting alcohol, which has a similar boiling point, were monitored by i.r. spectroscopy. For quantitative evaluation, measurements were performed in CCl_4 (cell 2 cm, conc. 3.5×10^{-3} mol l); bands 3550 cm^{-1} (OOH) and 3610^{-1} (OH) were used in the investigation. The amount of impurities present in the individual hydroperoxides was calculated from the extinction coefficient determined for 2,4,6-trimethyl-2-heptanol. The hydroperoxide content was also determined iodometrically. The characteristics of the hydroperoxides thus obtained are summarized in Table 1. The structures were confirmed by NMR spectroscopy. 2,6-Ditert-butyl-4-methylphenol, m.p. 69° .

Alkylperoxycyclohexadienones VIIa-VIIe

Alkylhydroperoxides II-VI (0.3 mole) were added at 80° with stirring to a benzene solution of 2,6-ditert-butyl-4-methyl-phenol (0.1 mole); after the temperature had become stable, 1 ml of a 2% solution of cobalt (II) acetyl acetonate in ethyl acetate was added. The reaction proceeds with a change in colour: the original colourless solution turns green when the catalyst has been added, and then gradually becomes green-yellow. The reaction was followed by means of TLC in the systems heptane:ether: CH_2Cl_2 5:1:1 and petroleum ether:ether:ethyl acetate 30:5:1. The reaction was interrupted after the starting phenol had disappeared. The reaction mixture was filtered; the solvent and unreacted alkylhydroperoxide (or its transformation products) were removed by prolonged evacuation at $60-80^\circ$ to constant weight. The viscous oil thus obtained was dissolved in methanol and extracted several times with a small amount of heptane. The heptane solution was concentrated on a rotary evaporator; the oil was dissolved in hot methanol and left to crystallize in the

refrigerator or in the case of VIIa,b,d with dry ice. These compounds crystallize at -78° but the crystals melt at room temperature. Crystallization from methanol was repeated until constant melting point was reached; the purities of liquid compounds were checked chromatographically. The characteristics of isolated pure VIIa-e are given in Table 2. NMR spectra and mass spectroscopic results are in agreement with the proposed structures.

Determination of the effect of alkylperoxycyclohexadienones on the oxidation of tetralin

The abilities of compounds of type VIII to influence the oxidation of tetralin were investigated by measuring oxygen absorption at $120 \pm 0.5^\circ$, using method described earlier papers [4,5]. Tetralin was oxidized in pure oxygen. Concentration of the additives was 3.3×10^{-4} mole l^{-1} but in some cases also 6.6×10^{-4} mole l^{-1} . From the absorption curves thus obtained, $\tau_{0.025}$ and $\tau_{0.125}$ respectively were read off as times needed for the absorption of 0.025 or 0.125 mole oxygen per mole of tetralin. The relative activities A_r were calculated for both τ values from the relationship $A_r = \tau_0/\tau_a$, where τ_0 refers to pure tetralin and τ_a to tetralin with additive. For the intercept of the absorption curve restricted by $\tau_{0.025}$ and $\tau_{0.125}$, the slopes $S = 1/(\tau_{0.125} - \tau_{0.025})$ and the relative values $S_r = S_a/S_0$ (ratio of slopes for tetralin with and without additive) were calculated.

RESULTS AND DISCUSSION

Alkylhydroperoxides II-VI used in the study of the transformation of the phenolic antioxidant are better than tert-butylhydroperoxide as models for hydroper-

Table 2. Characteristics of 2,6-ditert-butyl-4-alkylperoxy-4-methyl-2,5-cyclohexadienones VIIa-e, prepared at the molar ratio hydroperoxide-antioxidant 3:1

| Compound | Reaction time, hr | Yield | Calc./%C | Molecular formula (molecular weight) | Calc. %C | Found %H | λ_{max} , nm (log ϵ) | $\nu_{\text{C=O}}$ cm^{-1} | t , $^\circ\text{C}^*$ |
|----------|-------------------|-------|-----------|---|-----------------|-----------------|--|--|--------------------------|
| VIIa | 1.5 | 64 | † | $\text{C}_{23}\text{H}_{40}\text{O}_3$ (364.6) | 75.77/ 75.56 | 11.06/ 11.10 | 235 (4.049) 375 (1.363) | 1645 1665 | 115 |
| VIIb | 0.5 | 77 | † | $\text{C}_{23}\text{H}_{40}\text{O}_3$ (364.6) | 75.77/ 75.55 | 11.06/ 11.07 | 235 (4.050) 375 (1.358) | 1645 1665 | 110 |
| VIIc | 0.75 | 80 | 45-46 | $\text{C}_{22}\text{H}_{38}\text{O}_3$ (350.5) | 75.38/ 75.44 | 10.93/ 11.07 | 234 (4.051) 375 (1.362) | 1645 1670 | 115 |
| VIIId | 1.5 | 66 | † | $\text{C}_{23}\text{H}_{44}\text{O}_3$ (392.6) | 76.48/ 76.36 | 11.30/ 11.33 | 235 (4.009) 375 (1.369) | 1645 1665 | 110 |
| VIIe | 1.0 | 61† | 35.5-36.5 | $\text{C}_{23}\text{H}_{44}\text{O}_3$ (392.6) | 76.48/ 76.49 | 11.30/ 11.47 | 235 (4.053) 375 (1.361) | 1646 1670 | 115 |

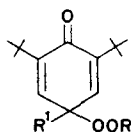
* Initial decomposition temperature determined by DSC.

† Molar ratio ROOH - antioxidant 2:1, product isolated by column fractionation.

‡ Liquid.

oxidized segments of the carbon chain of polyethylene or polypropylene. Interaction of 2,6-ditert-butyl-4-methylphenol with alkylperoxyls generated catalytically in benzene from the above hydroperoxides yielded 2,6-ditert-butyl-4-alkylperoxy-4-methyl-2,5-cyclohexadienones VIIIa–e. Thus, it was proved that cyclohexadienones of the ROOA' type were formed also in the reaction of the aryloxy A' or of its mesomeric form A'' with alkylperoxyls, in which the HOO- group is attached at various positions on a rather long carbon skeleton. Even comparatively high steric requirements of branched alkyls of some of the compounds used, predominantly in alkylperoxyls derived from alkyl hydroperoxides V and VI where the C₇ chain is branched at positions 2,4,6, do not greatly affect the reactivity (Table 2). With optimized conditions of synthesis, when the molar ratios of both reactants and the reaction times are adjusted for the individual compounds, the yields of all isolated alkylperoxycyclohexadienones are around 80%. The analytically determined (by LC) yields are higher. This means that, at a sufficient concentration of alkylperoxyls in the oxidized system hydrocarbon-phenolic antioxidant, alkylperoxycyclohexadienone is the main product. In the stoichiometric representation of reaction (1), under the conditions used one phenolic alkylated nucleus deactivates two alkylperoxyls. The phenolic antioxidant, which has not reacted to give alkylperoxycyclohexadienone, is subjected to other oxidation disproportionation and condensation reactions [1]. Deep-coloured compounds, for which a quinomethinoid structure is assumed according to earlier results, also appear among the products [7,8].

The synthetic result of the above model proof of the reactivities of various alkyl hydroperoxides characterizing the oxidized segment of branched polyethylene or polypropylene is also proof of the general reactivity of antioxidants possessing the basic structure of sterically hindered 2,6-ditert-butyl-4-substituted phenols. These compounds are comparatively readily transformed into 4-substituted derivatives of 4-alkylperoxy-2,5-cyclohexadienone. Mononuclear phenolic antioxidants (cf. also [2]) bisphenols [3], trisphenols [4,5] and tetrakisphenols [6] react in this way. The transformation of polynuclear phenolic antioxidants may proceed gradually, so that the products contain both the phenolic and cyclohexadienone skeletons.



- VIIIa, R = C(CH₃)₂C₅H₁₁, R¹ = CH₃
 VIIIb, R = C(CH₃)(C₂H₅)C₄H₉, R¹ = CH₃
 VIIIc, R = C(CH₃)₂CH₂CH(CH₃)CH₃, R¹ = CH₃
 VIId, R = C(CH₃)₂[CH₂CH(CH₃)]₂CH₃, R¹ = CH₃
 VIIIE, R = C(CH₃)[CH₂CH(CH₃)CH₃]₂, R¹ = CH₃
 VIIf, R = t - C₄H₉, R¹ = CH₃
 VIIIg, R = t - C₄H₉, R¹ = CH₂CH₂COOC₁₈H₃₇.

The properties of cyclohexadienones VIIIa–VIIIE investigated in this work were studied in greater detail; VIIf and VIIIg were used for comparison with the properties of systems already examined.

All VIIIa–e compounds contain in their i.r. spectra a double band 1645 cm⁻¹(s) and 1668 cm⁻¹(m), characteristic of 4-alkyl-substituted 2,5-cyclohexadienones [10]. The individual compounds exhibit a maximum shift of ± 2 cm⁻¹ due to structural differences. These bands were also observed with all 4-alkylperoxy-2,5-cyclohexadienones isolated earlier and derived from commercial antioxidants Irganox® 1010 [9] and 1076 [2], Ionox® 330 [4], and Good Rite® 3114 [5]. The spectral range 800–1250 cm⁻¹, which is useful in connection with peroxidic bond in the molecule, in the compounds under study has characteristic bands at 880, 1020, 1060, and 1246 cm⁻¹.

In the u.v. absorption of VIIIa–e, one can see an intensive band 210–255 nm with maximum within 233–235 nm (depending on the structure of the substituents). The band is typical of 2,5-cyclohexadienones [10]. A weaker diffuse band overlapping with the visible spectral region of these compounds is 325–425 nm with an indistinct maximum at 375 nm. Obviously, because of this absorption, all compounds containing the alkylperoxycyclohexadienone structure are very sensitive to daylight.

The mass spectrum of VIIIa–e exhibited only peaks of fragments; molecular ions could not be ascertained because of premature decomposition.

The thermal behaviour of alkylperoxycyclohexadienones was investigated in order to obtain data on their thermal stabilities. The DSC characteristics (Du Pont 900 Thermal Analyzer rate of heating 10° min⁻¹) of all compounds under investigation are very similar. Curves obtained with crystalline compounds exhibit well-characterized melting endotherms and subsequent endotherms of decomposition, which start between 110–115°. These values are not much affected by the alkyl structure in the alkylperoxyl group at position 4. It should be pointed out that the decomposition temperatures are generally lower than those for VIIf (125°) or VIIIg (120°).

For the ageing of polyolefins, it is important to know the effect of the products derived from the original antioxidant on the thermal oxidation of the hydrocarbon substrate. The alkylperoxycyclohexadienone derivatives possess properties of peroxidic initiators of the thermal process. Since these compounds had to be homogenized with the substrate without decomposition, a low-molecular weight liquid hydrocarbon had to be used. In the measurements performed up to now, we found that below the decomposition temperature compounds of the ROOA' type did not exhibit appreciable initiation effect [11] although even at these temperatures there is slow decomposition [12]. At temperatures near the decomposition point, a fast initial absorption of oxygen appears at concentrations approaching those of the originally present phenolic antioxidant [4,5,11].

The ability of 4-alkylperoxy-2,5-cyclohexadienones VIIIa–e to affect oxidation was examined by measuring oxygen absorption in tetralin. All measurements were carried out at 120°, i.e. at a temperature somewhat higher than that of the initial decomposition of the compounds under investigation. Typical absorption curves are given in Fig. 1. All additives of type VIII accelerate the oxidation of tetralin (Table 1). Their initiation activity is especially pronounced

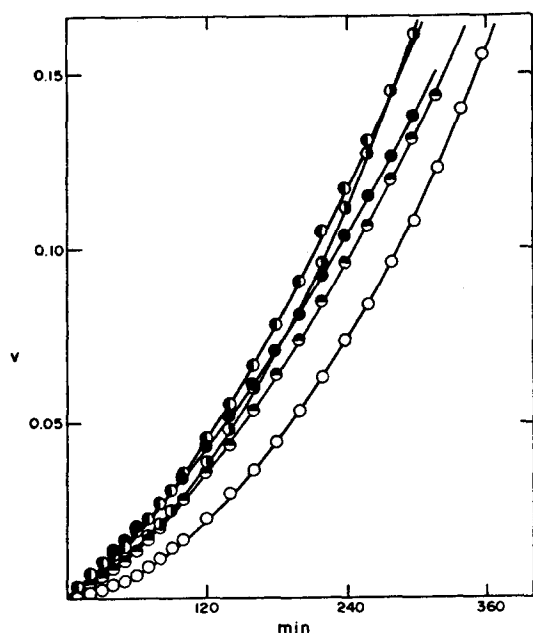


Fig. 1. Absorption curves of oxygen in the oxidation of tetralin (v = mole O_2 /mole tetralin) in the presence of 3.3×10^{-4} mole/l $^{-1}$ 4-alkylperoxy-2,5-cyclohexadienones at 120°C: ● VIIIa, ● VIIIc, ● VIIIe, ● VIIIg, ○ without additive.

in the initial stages. To compare the individual additives, relative activities A_r and the ratios of the slopes of curves in the investigated absorption region S_r were calculated for two characteristic regions of oxygen absorption (Table 3). The usual concentration of additive was 3.3×10^{-4} mole/l $^{-1}$. In the evaluation of the effect on oxygen absorption according to A_{r1} (in the initial stage of oxidation for absorption of 0.025 mole O_2 /mole tetralin) the abilities to accelerate oxidation lie in the series VIIIa, VIIIg, VIIIb < VIIIc, VIIIe < VIIIc, VIIIg. As in the consideration of DSC data with respect to the single variable structure unit, i.e. the alkyl group in the alkylperoxy group, there is no pronounced effect of structure of the alkyl group upon the course of oxidation. In all cases, the alkyl is bonded to the peroxidic oxygen atom through a

carbon atom, which is fully substituted with methyls or higher alkyls; consequently steric conditions are very similar. In principle, the effect of the alkyl in VIII can be characterized by saying that the weakest initiation activity is exhibited by derivatives with a group having the lowest degree of branching (VIIIa,b) derived from hydroperoxides belonging to the branched "polyethylene" type. Compounds possessing a strongly branched alkyl derived from hydroperoxides of the "polypropylene" type are more active. For characterization purposes, compounds possessing a longer carbon moiety in the alkylperoxy group are of importance (VIIIc,d,e). The first two of them were the most active of the whole group, and there was virtually no difference between their influences.

If activities are compared at a later stage of oxidation (A_{r2} , Table 3), the order of the compounds (VIIIa-e) is unchanged.

Interesting behaviour is observed with VIIIg. If studied in the region A_{r2} , VIIIg can be compared with VIIIe (transformation model of the antioxidant with hydroperoxide of the polypropylene type). In further oxidation, however, the presence of VIIIg causes such acceleration of the absorption of oxygen that it surpasses even the originally most active VIIIc. The main difference in the role or the structural elements in VIIIg is due to the presence of the functional group in the substituent R^1 , while in the case of all the other compounds R^1 is the methyl group. Although the functional group lies comparatively far from the carbon atom C_4 , to which the alkylperoxy group is bonded, its induction effect probably is operative. In this connection, one should note the different behaviour of VIIIg compared with all the other compounds of type VIII in TGA: the thermal decomposition of VIIIg is gradual and stepwise (Fig. 2). The initial drop of weight within the temperature range 135–180° corresponds to the splitting of the peroxidic bond in VIIIg. The remaining part of the molecule undergoes slow thermal decomposition compared with other compounds of type VIII, which exhibit simpler TGA curves; it is also characteristic of these compounds that the loss in weight is half the original value even at 165–170°. One half of the original VIIIg did not decompose until 305°.

Table 3. Activity of alkylperoxycyclohexadienones VIIIa–VIIIg in the oxidation of tetralin at 120°C; meaning of symbols see Experimental

| Compound | c^* | A_{r1}^\dagger | A_{r2}^\dagger | S_r |
|----------|-------|------------------|------------------|-------|
| VIIIa | c_1 | 1.39 | 1.13 | 1.02 |
| | c_2 | 2.07 | 1.31 | 1.06 |
| VIIIb | c_1 | 1.47 | 1.14 | 1.00 |
| VIIIc | c_1 | 1.95 | 1.34 | 1.12 |
| | c_2 | 2.32 | 1.36 | 1.08 |
| VIIIe | c_1 | 2.00 | 1.36 | 1.14 |
| VIIIe | c_1 | 1.75 | 1.27 | 1.08 |
| VIIIg | c_1 | 1.72 | 1.17 | 1.00 |
| | c_2 | 2.24 | 1.37 | 1.10 |
| VIIIg | c_1 | 1.43 | 1.26 | 1.18 |
| | c_2 | 2.38 | 1.55 | 1.28 |

* Concentration $c_1 = 3.3 \times 10^{-4}$ mole/l $^{-1}$; $c_2 = 6.6 \times 10^{-4}$ mole/l $^{-1}$.

† Indexes 1 and 2 hold for $\tau_{0.025}$ and $\tau_{0.125}$ respectively.

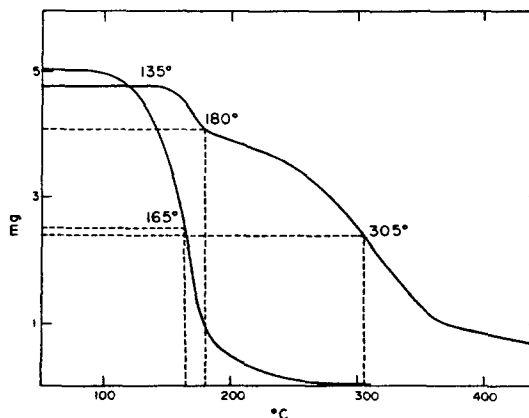


Fig. 2. TGA curves of VIIIc and VIIIg (measured with a Du Pont 950 Thermogravimetric Analyzer, rate of heating 10° min $^{-1}$, sensitivity 1 mg in $^{-1}$).

A representative of the most active and one of the least active of the newly synthesized compounds of type VIII were taken and investigated at a twofold concentration (6.6×10^{-4} mole/l $^{-1}$). The relative activities A_{r1} and A_{r2} were again in the order VIIIa < VIIIb, VIIIc < VIIf. The alkyl R in the alkylperoxy group of compounds in which R¹ is methyl is again operative as at lower concentration. Under such concentration conditions, VIIf is the most active initiator from the very beginning, and its behaviour is therefore specific in this case also.

It can be concluded that all compounds of type VIII under investigation accelerate the initial stage of the oxidation of tetralin at 120° owing to their thermal instability; their activities at lower concentration lie within the range A_{r1} 1.39–2.00. In the later stages, compounds which permanently accelerate oxidation (VIIf–e,g) become markedly different from compounds which practically do not affect the further course of oxidation (VIIIa,b,f). The results can be extrapolated to the behaviour of alkylperoxycyclohexadienones in polyolefins.

Acknowledgements—We thank our colleagues from the Institute for measurements of spectra and for elemental ana-

lyses. Technical assistance was carefully provided by Mrs M. Kremličková.

REFERENCES

1. J. Pospíšil, *Pure appl. Chem.* **36**, 207 (1973).
2. J. Lerchová and J. Pospíšil, *Chem. Ind.* 516 (1975).
3. L. Taimr, H. Pivcová and J. Pospíšil, *Colln. Czech. chem. Commun.* **37**, 1912 (1972).
4. J. Lerchová and J. Pospíšil, *Angew. Makromol. Chem.* **38**, 191 (1974).
5. J. Lerchová and J. Pospíšil, *Angew. Makromol. Chem.* **39**, 107 (1974).
6. A. G. Davies and R. V. Foster, *J. chem. Soc.* 1541 (1953).
7. L. Taimr and J. Pospíšil, *Angew. Makromol. Chem.* **28**, 13 (1973).
8. J. Lerchová, G. A. Nikiforov and J. Pospíšil, *15th Prague Microsymposium Degradation and Stabilization of Polyolefins*, Paper F5, Prague, July 21–24 (1975).
9. J. Kovářová-Lerchová and J. Pospíšil, unpublished results.
10. A. J. Waring, Cyclohexadienones, in: *Advances in Alicyclic Chemistry* (edited by H. Hart and G. J. Karabatsos), Vol. 1. Academic Press, New York (1966).
11. I. Buben and J. Pospíšil, *Colln. Czech. chem. Commun.* **40**, 977, 987 (1975).
12. I. Buben and J. Pospíšil, *J. Polym. Sci., Polym. Symposia*, to be published.