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Cationic Polymerization of 2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone and Photostabilizing Efficiency of Oligomer in Polypropylene

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ABSTRACT

The polymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone catalyzed by tin(IV) chloride in a solution of chloroform and dichloromethane was investigated by adiabatic calorimetry, and the photostabilizing efficiency of the product of the polymerization in polypropylene fibers was estimated. The kinetic study has shown that the amount of catalyst rapidly decreases during the reaction, the time decrease in the concentration of active centers involves their rapid deactivation, and an oligomer with a low degree of polymerization arises. No distinct destruction of the 2-hydroxybenzophenone structures appears during the cationic polymerization as indicated by the UV spectra and the results of measurements of the photostabilizing efficiency. In comparison with 2-hydroxy-4-n-octyloxybenzophenone, the higher molecular stabilizer thus prepared exhibits lower extractibility from polypropylene fibers with ligroin.

INTRODUCTION

The study of the syntheses and the effect of polymer light stabilizers on the basis of the derivatives of 2-hydroxybenzophenone has shown

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that the anionic polymerization of 2-hydroxy-4-(2,3-epoxypropoxy)-benzophenone (HEB) does not give the required products. It has been revealed by NMR, IR, and UV spectral analysis that the anionic polymerization of HEB does not proceed via polymerization of the epoxide group but the phenolic group [1] bonded by a hydrogen bond is destroyed and thus participates in the growth reaction. The reactivity of the phenolic group in the anionic process has also been verified by the model reaction of 2-hydroxybenzophenone with 2-(2,3-epoxypropoxy)benzophenone. In the presence of an excess of the first compound, 2-hydroxybenzophenone structures [2] are partially destroyed, similar to the anionic copolymerization of HEB cyclic anhydrides of dicarboxylic acids. The result of these reactions is an impairment of poly(HEB) as a polymer light stabilizer.

The proposed scheme of the anionic polymerization of HEB shows [1] that the abstraction of hydrogen of the phenolic group by the strongly basic alkoxide anion is more rapid than an interaction of anion with an epoxide group giving rise to "normal" polyether and thus the anionic polymerization is not suitable for the polymerization of epoxides containing a proton-donating group in a molecule. The chemical character of this process enables us to assume that the "normal" polymer could be prepared by cationic polymerization of HEB in a molecule of which the quasi-chelate arrangement of groups conditioning the light stabilizing effect of the derivatives of 2-hydroxybenzophenone should be preserved. Tin(IV) chloride, which does not require the addition of other components, was used as catalyst.

The mechanism of the polymerization of epoxides catalyzed by $SnCl_4$ was suggested by Eastham [3]. The progress of the polymerization of ethylene oxide was investigated by Worsfold and Eastham who established that tin(IV) chloride initiated the growth of the two polymer chains and the propagation proceeded via an intermediary oxonium ion while the termination was governed by destruction of the catalyst [4]. The polymerization of propylene oxide with the catalytic system $SnCl_4$-acetyl chloride was studied by Sakai et al. [5]. Their results are consistent with the idea that $SnCl_4$ coordinately activates two molecules of epoxide. The formation of the two active centers in the $SnCl_4$ molecule was also found in the polymerization of epichlorohydrin. In this case, the amount of the catalyst used was completely bonded to active centers during the very fast initiating reaction [6].

In this paper the results of the study of ring-opening polymerization of HEB by the effect of $SnCl_4$ in solutions of chlorinated solvents are presented. The method using the released reaction heat for investigating the progress of reaction was applied at extremely high polymerization rates. Furthermore, the photostabilizing efficiency of the oligomer of HEB in polypropylene fibers and the washability of this stabilizer from polypropylene fibers by ligroin extraction were evaluated.

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EXPERIMENTAL

Materials

2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone was synthetized from 2,4-dihydroxybenzene and epichlorohydrin [2], mp = 99-100°C. After drying in vacuo at 90°C, it was stored in a desiccator over P_2O_5.

Analytical grade tin(IV) chloride (Lachema, N. E. Brno, CSSR) was distilled in vacuo before use.

Analytical grade chloroform and dichloromethane (Lachema, N. E. Brno, CSSR) were purified with concentrated H_2SO_4 and subsequently with a dilute solution of NaOH and H_2O [7]. The washed material was dried over P_2O_5 and subjected to fractional distillation in an atomosphere of dry nitrogen.

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Apparatus and Polymerization Procedure

The polymerizations were carried out at 20°C in a glass calorimeter with a vacuum jacket. The capacity of this calorimeter was about 250 mL. It was equipped with a mechanical stirrer, thermometer, adapter for adding the catalyst, inlet and outlet of dry nitrogen, and a thermistor of the type 11 NR 15 (ZPP, Sumperk, CSSR) connected to a Wheatstone bridge. The external jacket of the reactor was temperature-controlled with a water thermostat at 20 ± 0.1°C and the calorimeter was installed in a temperature-controlled room. The temporal course of the output voltage proportional to the measured temperature change in the reaction mixture was recorded with an RE 511 recorder (Kompensationsschreiber Goerz Elektro, Austria). The time constant for the thermistor connected to the recorder was 0.7 s. The heat capacity of System C, consisting of a solution of monomer in dried chloroform or dichloromethane, was determined electrically.

The reactor was purified with chromatosulfuric acid and hot water, dried, and bubbled with dried nitrogen before use. The solution of monomer (100 mL) in dry solvent, the temperature of which was by 1-2°C higher than necessary for the reaction, was added into the colorimeter and the system was thermostatted to constant temperature varying only in the range ± 0.01°C/min. Then the necessary volume of the thermostatted catalyst (or its concentrated solution in $CHCl_3$ or CH_2Cl_2) was quickly added into the solution of monomer by means of a microsyringe with a long needle. The time course of the temperature difference ΔT in the reaction mixture was recorded with a recorder. Small temperature changes $\Delta T'$ due to the heat of mixing of $SnCl_4$ with solvent and the reaction with impurities in solvents were determined analogously. When the monomer conversion was investigated, the time course ΔT was corrected for the values of

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$\Delta T'$. The polymerization in particular reaction systems was stopped by adding 20-50 mL of a 3% solution of ammonia in methanol. After evaporation of solvents, the product was extracted with a solution of methanol containing 20% water (by volume) and subsequently three times with methanol at 60°C. In order to estimate the conversion, the oligomer was dried to constant weight in vacuo at 90°C.

The heat capacity of System C does not practically change during monomer polymerization in a very dilute solution if a small amount of polymer arises. The quantity of heat dq evolved in the monomer polymerization dm in the time dt accumulates in the reaction system, causing a temperature rise in the system of $d(\Delta T - \Delta T')$ while the heat of the rapid reaction given up to environs from a practically adiabatic system in the time interval of a few minutes may be neglected. The kinetic measurements were based on the heat balance and the investigated system is governed by

$$\frac{dq}{dt} = C\frac{d(\Delta T_c)}{dt} = -\frac{dm}{dt}\Delta H_p \qquad (1)$$

where ΔH_p is the heat of polymerization and $\Delta T_c = \Delta T - \Delta T'$.

By integrating Eq. (1) and taking into account interactions of the catalyst with solvent, the degree of conversion $m_0 - m$ was evaluated. It is given by

$$m_0 - m = \frac{C}{\Delta H_p}(\Delta T_c) \qquad (2)$$

where m_0 and m are the initial monomer concentration and the monomer concentration in the course of the reaction, respectively. The heat of polymerization ΔH was determined from the known values of conversion after the heat capacity of the system had been found.

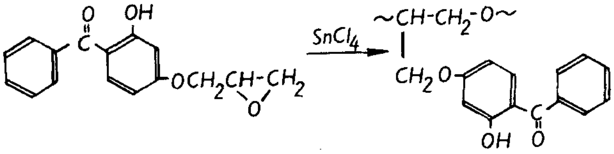
Determination of the Photostabilizing Efficiency

The stabilizing efficiency was evaluated according to the method [8] based on the measurement of the volume of oxygen consumed in photooxidation of 0.1 g of stabilized polypropylene fibers. The polypropylene fibers were prepared by spinning polypropylene Tatren TF-111 (Slovnaft, N. E. Bratislava) containing 0.1 wt% of 2,6-ditert-butyl-4-methylphenol, 0.35 wt% of β,β'-dilauryl thiodipropionate, 0.15 wt% of calcium stearate, and 0.3 wt% of light stabilizers. The fibers were prepared at 270°C using spinning equipment with a feed of the polymer melt (15 g/min) through a die with 20 holes (0.5 mm diameter) at a spinning rate of 422 m/min. The prepared fibers were drawn to a 1:4 ratio and the titer of the stabilized fibers was 122.8 dtex.

The stabilizing effect of the oligomer HEB was compared with the efficiency of 2-hydroxy-4-n-octyloxybenzophenone in original fibers as well as fibers washed three times with ligroin at laboratory temperature. The fibers (0.1 g each) were extracted in each washing for 40 min in 50 mL of ligroin and dried for 24 h in air.

RESULTS AND DISCUSSION

The synthesis of higher-molecular light stabilizers based on HEB with reduced extractibility requires the 2-hydroxybenzophenone structural units exhibiting the photostabilizing effect not to be disturbed. One of the possibilities is the cationic polymerization of HEB catalyzed by $SnCl_4$ in a solution of chlorinated hydrocarbons:



The typical kinetic curves representing the time dependence of the degree of conversion obtained from the time course of the temperature differences at varying concentrations of HEB and $SnCl_4$ and corrected according to Eq. (2) are given in Fig. 1 for the reaction in a solution of chloroform and dichloromethane. The gravimetrically determined values of the degree of conversion of HEB and the heat capacity of System C (198 kJ/K in a solution of chloroform) were used for calculation of the polymerization heat ΔH_p (79 ± 8 kJ/mol) by means of Eq. (2). An increase in the initial concentration of the monomer with respect to the catalyst leads to an increase in the degree of monomer conversion. The reaction rate rapidly decreases during polymerization and a considerable portion of the monomer remains nonconsumed after the reaction has stopped. The final degree of conversion increases with the initial concentration of the catalyst which is evidently consumed in the reaction. The polymerization is slower in chloroform than in dichloromethane, even in the initial stage. This effect is in accordance with the generally accepted view that the rate of cationic polymerization decreases with increasing dielectric constant of the solvent.

Because of the nonstationary course of the reaction, the reaction order was determined at 20°C from the initial polymerization rate v_0

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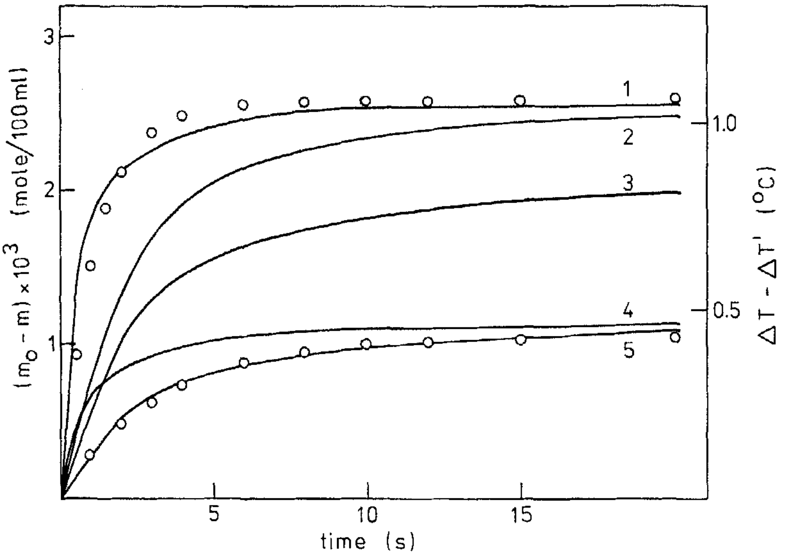

FIG. 1. Time dependence of the degree of conversion $m_0 - m$ or $\Delta T - \Delta T'$ (corrected temperature difference) in cationic polymerization of HEB catalyzed by $SnCl_4$ in chlorinated hydrocarbons (initial concentrations of HEB and catalyst expressed in mol/100 mL total volume reaction mixture are m_0 and c_0, respectively). Points stand for the values calculated according to Eq. (13) (1) $m_0 = 0.01$, $c_0 = 0.0015$ in CH_2Cl_2; (2) $m_0 = 0.01$, $c_0 = 0.0015$ in $CHCl_3$; (3) $m_0 = 0.015$, $c_0 = 0.001$ in $CHCl_3$; (4) $m_0 = 0.01$, $c_0 = 0.0005$ in CH_2Cl_2; (5) $m_0 = 0.01$, $c_0 = 0.0005$ in $CHCl_3$.

while the initial concentrations of epoxide and catalyst were m_0 and c_0, respectively. The experimental results given in Table 1 give an approximate relation for the polymerization in chloroform or dichloromethane

$$v_0 = km_0^{0.15}c_0^{0.85} \qquad (3)$$

The rate constant k in Eq. (3) for the polymerization in chloroform or dichloromethane has the values of 0.42 and 1.2 s^{-1}, respectively. If the polymerization of HEB stops before all monomer has been consumed, it means that the rate of termination is not negligibly small compared with the rate of propagation. Then the ratio of the rate constants for propagation and termination k_p/k_t does not reach a high value and a polymer with low molecular weight is obtained [9].

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TABLE 1. Variation of the Initial Polymerization Rate v_0 with the Initial Concentrations of HEB (m_0) and $SnCl_4$ (c_0) in Chlorinated Hydrocarbons and the Values of Maximum Conversion and Maximum Temperature Difference after Stopping of the Polymerization

m_0 (mol/L)	$c_0 \times 10^2$ (mol/L)	$v_0 \times 10^2$ ($mol \cdot L^{-1} \cdot s^{-1}$)		Maximum yield (%)		$\Delta T - \Delta T'$[c] (°C)	
		$CHCl_3$[a]	CH_2Cl_2[b]	$CHCl_3$	CH_2Cl_2	$CHCl_3$[d]	CH_2Cl_2[d]
0.25	1.0	0.56	2.10	9.2[e]	8.6[f]	0.88	0.94
0.20	1.0	0.55	2.11	10.3	10.9	0.85	0.90
0.15	1.0	0.53	1.98	13.1	14.0	0.81	0.86
0.10	1.0	0.50	1.85	17.6	19.5	0.72	0.80
0.10	0.25	0.17	0.68	6.8	6.6	0.28	0.27
0.10	0.5	0.26	0.97	10.8	11.2	0.44	0.46
0.10	0.75	0.39	1.44	14.3	15.3	0.59	0.63
0.10	1.5	0.78	2.62	24.6	25.5	1.01	1.05

[a] $v_0 = 0.42 m_0^{0.12} c_0^{0.9}$.

[b] $v_0 = 1.2 m_0^{0.15} c_0^{0.83}$.

[c] For initial concentrations m_0 and c_0 in mol/100 mL reaction mixture.

[d] Temperature differences $\Delta T'$ (0.03-0.11°C) due to the interaction between catalyst and solvents.

[e] M_n = 1190, measured by VPO method with $CHCl_3$ as solvent.

[f] M_n = 1210.

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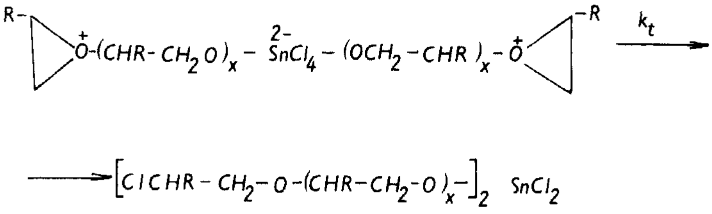
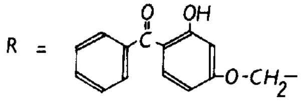
If the active centers P_n^+ decay during polymerization, intramolecular deactivation can be assumed:





On this basis, the termination is the first-order reaction

$$-d[P_n^+]/dt = k_t[P_n^+] \tag{4}$$

The catalyst $SnCl_4$ of the initial concentration c_0 generates two reaction centers [3] with efficiency f in the initiation reaction. Thus the initial concentration of the initiating centers $[P_n^+]_0$ can be expressed by the equation

$$[P_n^+]_0 = 2fc_0 \tag{5}$$

The time loss of the active centers is defined by

$$[P_n^+] = 2fc_0e^{-k_tt} \tag{6}$$

By inserting Eq. (6) into the rate equation of polymerization

$$-dm/dt = k_pm[P_n^+] \tag{7}$$

and integrating, we obtain the resulting relation for the time course of polymerization:

$$\ln \frac{m_0}{m} = \frac{k_p}{k_t} 2fc_0(1 - e^{-k_t t}) \tag{8}$$

After the stopping of polymerization ($[P_n^+] = 0$), the residual concentration of monomer m_f remains unconsumed and Eq. (8) assumes the form

$$0.5 \ln \frac{m_0}{m_f} = \frac{k_p}{k_t} fc_0 \tag{9}$$

Considering termination to be the first-order reaction, we can determine the ratio fk_p/k_t from Eq. (9) if the efficiency factor f does not significantly change with varying concentrations of the monomer and the catalyst used [9].

Taking into account Eqs. (5) and (7), we obtain for the initial rate of polymerization

$$v_0 = 2fk_p m_0 c_0 \tag{10}$$

and using Eqs. (3) and (10) we may write

$$2fk_p = k/(m_0^{0.85} c_0^{0.15}) \tag{11}$$

It is evident from this expression that the efficiency factor is dependent on the initial concentrations of the reacting components.

By inserting Eq. (11) into Eq. (9), we obtain

$$c_0^{0.15} \ln \frac{m_0}{m_f} = \frac{k}{k_t} \frac{1}{m_0^{0.85}} c_0 \tag{12}$$

By using the constant concentration m_0, the experimental values of the concentration of the unconsumed monomer m_f after polymerization stops and the varying concentrations of the catalyst, we may determine the value of the termination constant on the basis of graphical analysis of Eq. (12).

The following expression results from Eqs. (8) and (11):

$$\ln \frac{m_0}{m} = \frac{k}{k_t} \left(\frac{c_0}{m_0}\right)^{0.85} (1 - e^{-k_t t}) \tag{13}$$

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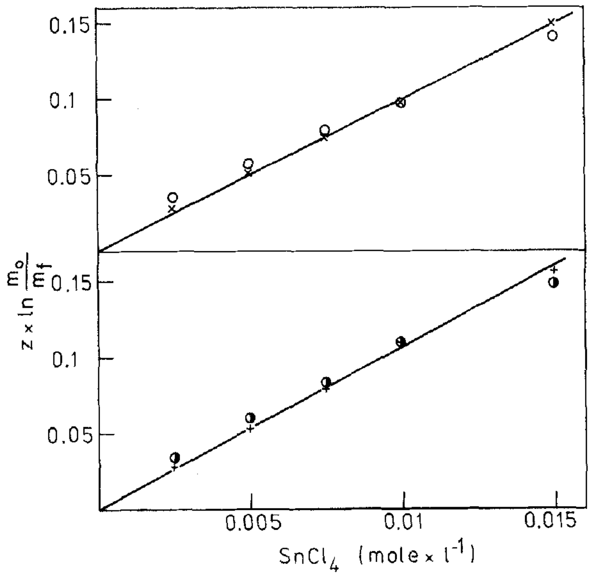

FIG. 2. Determination of fk_p/k_t or k/k_t for the polymerization of HEB according to Eq. (9) [(o) –$CHCl_3$, (◑) –CH_2Cl_2 (z = 0.5)] and according to Eq. (12) [(x) –$CHCl_3$, (+) –CH_2Cl_2 ($z = c_0^{0.15}$)].

Some values calculated according to Eq. (13) and the corresponding experimental data are given in Fig. 1.

Figure 2 shows the correlation of the experimental results obtained in the polymerization of HEB (m_0 = 0.1 mol/L) catalyzed by $SnCl_4$ (c_0 = 0.0025-0.015 mol/L) in chloroform and dichloroethane at 20° C with the values calculated from Eq. (12). For comparison, the functional relationships according to Eq. (9) are also given in Fig. 2. However, they describe the linear course less satisfactorily. The termination constants k_t found from the slope of the linear relation (Eq. 12) have the values of 0.3 and 0.8 s^{-1} for the polymerization in $CHCl_3$ and CH_2Cl_2, respectively. The small values of fk_p/k_t found for the polymerization in $CHCl_3$ (9.8 L/mol) and CH_2Cl_2 (10.6 L/mol) indicate that no polymers with a higher degree of polymerization can be prepared in the polymerization system mentioned. Oligomers prepared by the polymerization of HEB catalyzed by $SnCl_4$ in chloroform or dichloromethane (m_0 = 0.25 mol/L and c_0 = 0.01 mol/L) exhibit low values of M_n after extraction with hot methanol (M_n = 1190 for polymerization in $CHCl_3$ and M_n = 1210 for polymerization in dichloromethane). These molecular weights correspond to oligomers with a degree of polymerization of 4 or 5.

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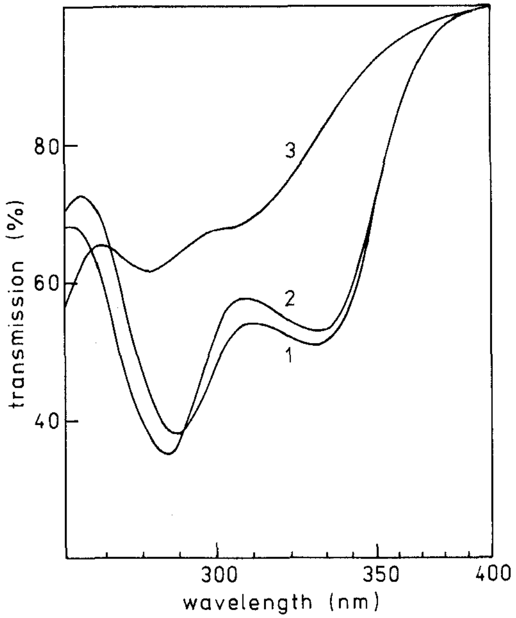

FIG. 3. Ultraviolet spectra of 2-hydroxy-4-n-octyloxybenzophenone (1), poly(HEB) prepared by cationic polymerization (2), and poly(HEB) prepared by anionic polymerization (3) in $CHCl_3$. Concentration 5×10^{-5} mol/L, cell width 0.5 cm.

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Poly(HEB) prepared by cationic polymerization has a UV spectrum analogous to that of the derivatives of 2-hydroxybenzophenone (Fig. 3) in contrast to the spectrum of poly(HEB) prepared by anionic polymerization where the band at the wavelength of 327 nm vanishes. This band corresponds to the carbonyl group bonded to the phenolic group by a hydrogen bond.

The oligomer prepared by the polymerization of HEB (0.25 mol/L) catalyzed by $SnCl_4$ (0.01 mol/L) was homogenized with polypropylene and the mixture was used for the preparation of fibers. The stabilizing effect was investigated in fibers subjected to accelerated aging. The experiments were performed with original samples and samples extracted once or three times with ligroin. The efficiency was compared with that of low-molecular stabilizer, i.e., 2-hydroxy-4-n-octyloxybenzophenone. The results are in Fig. 4. This figure shows that the efficiency of the polyether of HEB in the original sample is lower than that of the standard. This effect can only partially be explained by a lower extinction coefficient (Fig. 3). Another possible explanation of the lower efficiency of poly(HEB) consists in the reduced mobility of the oligomer. While for low-molecular stabilizers even

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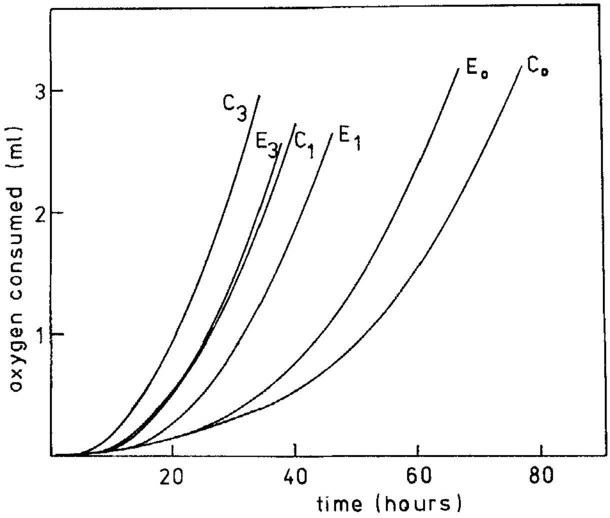

FIG. 4. Photoxidation of polypropylene fibers stabilized by 2-hydroxy-4-n-octyloxybenzophenone (C) and poly(HEB) (E) prepared by cationic polymerization in the original fibers (C_0, E_0), after one extraction with ligroin (C_1, E_1), and after three extractions with ligroin (C_3, E_3).

the monomolecular distribution of the stabilizer in the amorphous phase of the polymer may be expected, the local concentration of the stabilizing structures is higher for the polymer types of stabilizers owing to their polymer character. This idea enables us to assume the lower concentration of the stabilizing units in the proximity of the more concentrated microregions and thus to explain the more rapid course of aging.

On the other hand, the efficiency of the oligomer stabilizer after extraction with ligroin is higher than that of the standard. This means that the washability of the low molecular stabilizer is higher than that of the polymer stabilizer. However, as has already been stated [10], the use of oligomer stabilizers does not fully eliminate but only reduces the physical loss of stabilizers during the washing of polymers. From the viewpoint of the reduction of the physical loss of stabilizers, better results may be obtained if polymer stabilizers with M_n = 15,000-20,000 are used [11] or stabilizing units are built in the structure of the polymer [12].

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