

# Compatibility of photostabilizers with isotactic polypropylene\*

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Compatibility of two homological series of photostabilizers: 2-hydroxy-4-*n*-alkoxybenzophenones ( $n = 1, 2, 4, 8, 12$  and 18) and 2(2'-hydroxy-5'-*n*-alkylphenyl)benzotriazoles ( $n = 1, 2, 4, 8$  and 12) with crystalline isotactic polypropylene has been studied by the method of melting point depression and isothermal crystallization, respectively. It was found that with increasing number of carbon atoms in the alkoxy and alkyl chain of the stabilizers their compatibility with polypropylene improved. The values of the heat of fusion per repeating unit of polymer,  $\Delta H_u$ , prove to be for individual mixture in conjunction with the isothermal crystallization rate. The microphotographic observation of the mixtures confirms the increase of the mixture homogeneity along with the prolongation of the alkyl or alkoxy substituents of the photostabilizers.

Recently [1] we pointed out the importance of knowing a compatibility of a low-molecular additive with a crystalline polymer when used as stabilizer against degradation and ageing. In that paper we studied a compatibility of the above-mentioned series of 2-hydroxy-4-*n*-alkoxybenzophenones with crystalline polypropylene using the method of melting point depression.

In this paper the method of melting point depression is enriched with the investigation of differences in the crystallization rate of a polymer due to the presence of additives. This makes possible to obtain the data about the compatibility of components in the system. On the other hand the microphotographic observation of the course of isothermal crystallization enables us to obtain a direct view of dispersion of particular u.v. stabilizers in polymer.

## Experimental

### *Material and methods*

Crystalline polypropylene and 4-alkoxy derivatives of 2-hydroxybenzophenone (BPhC<sub>1-18</sub>) were described previously [1]. A series of 2(2'-hydroxy-5'-*n*-alkylphenyl)benzotriazoles referred to as PhBTC<sub>1-12</sub>, benzophenone (BPh), 2-hydroxybenzophenone

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(2-HOBPh) and 2(2'-hydroxyphenyl)benztriazole (2-HOPhBT) were supplied by the Research Department of the J. Dimitrov Chemical Works in Bratislava.

For thermal measurements, a Perkin-Elmer Differential Scanning Calorimeter Model DSC-1B was used. Sample preparation and measurement conditions for the method of melting point depression were described previously [1]. In the case of isothermal crystallization, mixtures containing 20% (v/v) of stabilizer were used. Annealing time was 10 minutes at 513 K. All measurements were carried out under a nitrogen atmosphere. Conditions of microphotographic observations were as follows: annealing time 5 minutes at 190°C, cooling rate 4°C/min, nitrogen atmosphere.

## Results

### Interaction energy

For the determination of interaction energy as a measure of compatibility in the system polypropylene-PhBTC<sub>1-12</sub> was used Flory's equation of melting point depression [2]

$$\frac{1/T_m - 1/T_m^0}{v_1} = \frac{RV_u}{\Delta H_u V_1} \left( 1 - \frac{BV_1 v_1}{R T_m} \right), \quad (1)$$

where  $V_u$  is the molar volume of the polymer repeating unit,  $V_1$  the molar volume of the diluent,  $\Delta H_u$  the fusion heat of the polymer repeating unit (cal/r.u.),  $v_1$  the volume fraction of the diluent and  $B$  the interaction energy density for the solvent-solute pair.  $T_m^0$  and  $T_m$  are the melting points of pure polymer and the mixture, respectively.

The obtained values of fusion heat,  $\Delta H_u$ , of the polymer and of interaction energy  $B$  are quoted in Table 1.

### Isothermal crystallization

For checking the compatibility of diluents, pigments, and some polymers with isotactic polypropylene, *Parrini* and *Corrieri* [3] proposed, on the basis of dilatometric measurement of crystallization of these mixtures, the following ratio

$$C = \tau_{0.5}/\tau_{0.5}^0,$$

where  $\tau_{0.5}$  and  $\tau_{0.5}^0$  are the half-lives of crystallization of the mixture and the pure polymer, respectively. The authors assume that a "good" *i.e.*, compatible diluent slows down the crystallization rate ( $C > 1$ ) while an incompatible one either has no effect or causes an increase in the crystallization rate ( $C \leq 1$ ). The ratio of half-lives of crystallization as a measure of compatibility has been used in this paper to characterize the particular pair polymer-stabilizer. However, these measurements were later supplemented by the determination of the ratio  $\tau_{0.9}/\tau_{0.9}^0$  *i.e.*, the ratio of the times when 1/10 of the whole amount of sample underwent crystallization. The value  $\tau_{0.9}$  makes possible to compare rationally the crystallization rates of mixtures of different composition, while the complications connected with the differences in supercooling in dependence on the composition of mixtures are avoided when crystallization proceeds isothermally. The course of initial parts of isotherms best corresponds to simplified mathematical formulation of kinetics of phase changes regardless of the composition of mixtures ([4]; p. 282).

Differential scanning calorimetry has many advantages compared to other methods of the study of isothermal crystallization (dilatometry, microscopy, and *i.r.* spectroscopy),

Table 1

The data of the heat of fusion and interaction energy density for the used mixtures of photostabilizers with crystalline polypropylene

Sample	$\Delta H_u$ [kcal mol <sup>-1</sup> ]	$B$ [cal cm <sup>-3</sup> ]
BPh + IPP*	0.95	7.8
PhBTC <sub>1</sub> + IPP	1.84	5.2
PhBTC <sub>4</sub> + IPP	1.19	4.9
PhBTC <sub>8</sub> + IPP	1.08	4.6
PhBTC <sub>12</sub> + IPP	1.93	-1.4

Isotactic polypropylene.

namely small size and fast establishment of thermal equilibrium. The positive contribution of the method of isothermal crystallization in comparison with that of melting point depression (when dealing with compatibility) becomes evident in the sense of the results being not influenced by the presence of amorphous part of polymer. The kinetic relation for calorimetric investigation of isothermal crystallization is given by [7]

$$1 - \Theta = \frac{\int_0^t \frac{d^1 \Delta H(t)}{dt} dt}{\int_0^{t_c} \frac{d \Delta H(t)}{dt} dt} = 1 - \exp(-kt^n) \quad (2)$$

where  $\Theta$  is the noncrystallized part of polymer,  $\Delta H$  the released heat,  $t_c$  is the time at the end of the process,  $k$  is the rate constant and  $n$  is the Avrami exponent which provides qualitative information on the nature of the nucleation and growth process.

To estimate the Avrami parameter  $n$  and the rate constant  $k$ , equation (2) is to be used in the following form

$$\log(-\log \Theta) = 0.434 \log k + n \log t. \quad (3)$$

DSC curves of isothermal crystallization and plots of  $\log(-\log \Theta) = f(\log t)$  and  $1 - \Theta = f(\log t)$  for mixtures PhBTC<sub>1-12</sub> with crystalline polypropylene are shown in Figs. 1-3.

The rate of isothermal crystallization of pure polypropylene and its mixture with

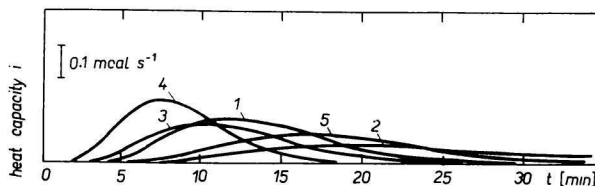


Fig. 1. DSC curves of isothermal crystallization of polypropylene with 20% (v/v) of photostabilizers PhBTC<sub>1-12</sub> in the mixture. Crystallization temperature 394 K.

1. PhBTC<sub>1</sub>; 2. PhBTC<sub>4</sub>; 3. PhBTC<sub>8</sub>; 4. PhBTC<sub>12</sub>; 5. PhBTC<sub>2</sub>.

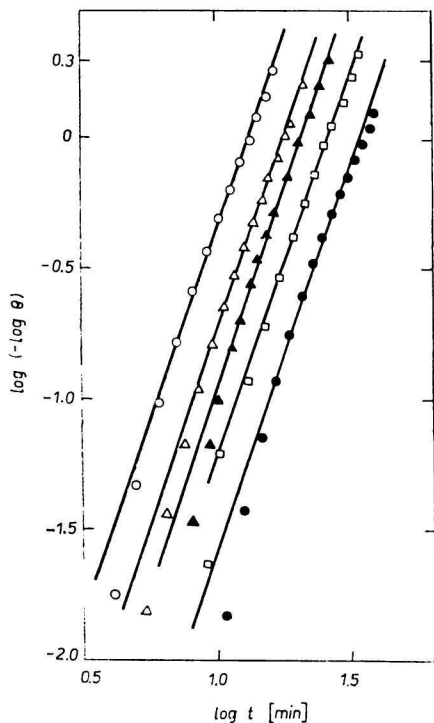


Fig. 2. Isothermal crystallization of polypropylene with 20% (v/v) of photostabilizers PhBTC<sub>1-12</sub> (394 K). Noncrystallized part of polymer as a function of time.

▲ PhBTC<sub>1</sub>; ● PhBTC<sub>4</sub>; △ PhBTC<sub>8</sub>;  
○ PhBTC<sub>12</sub>; □ PhBTC<sub>2</sub>.

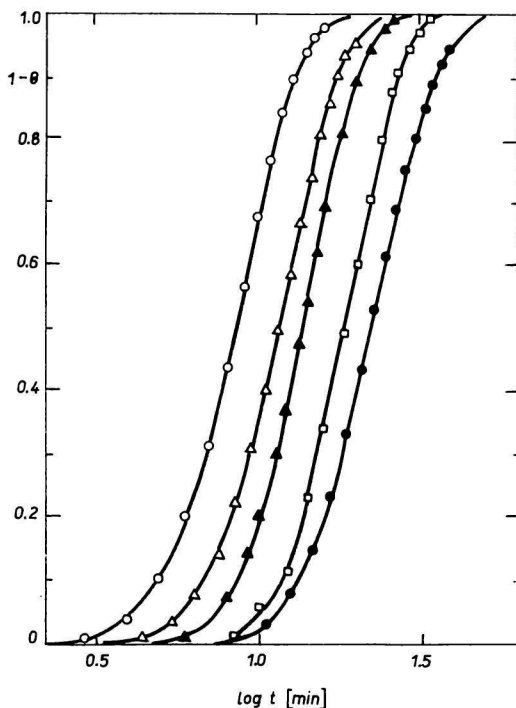


Fig. 3. Isothermal crystallization of polypropylene in the mixtures with 20% (v/v) of photostabilizers PhBTC<sub>1-12</sub> (394 K).

Relation of  $1 - \Theta$  vs.  $\log t$ .

▲ PhBTC<sub>1</sub>; ● PhBTC<sub>4</sub>; △ PhBTC<sub>8</sub>;  
○ PhBTC<sub>12</sub>; □ PhBTC<sub>2</sub>.

2-hydroxybenzophenone is at 394 K relatively high. Due to this fact it turned out to be impossible to scan the overall course of the crystallization. So the rate constants for this temperature were estimated by means of the following relations for crystallization of pure polymer ([4]; p. 225, 282) and of polymer in the presence of diluent [5]

$$\log k = f[T_m^2/T(\Delta T)^2],$$

$$\log 1/\tau_{0.9} = f[T_m^2/T(\Delta T)^2], \quad (4)$$

where  $k$  is rate constant,  $\tau_{0.9}$  is the time when 10% of polymer is being crystallized,  $T_m$  the melting point of polymer or of the mixture,  $\Delta T$  is the degree of supercooling. The courses of these dependences are shown in Figs. 4 and 5.

In Table 2 are summarized the data of kinetic parameters for individual samples. Dependences of the ratio  $\tau_{0.9}/\tau_{0.9}^0$  as a function of the number of carbon atoms in the alkoxy or alkyl substituents, respectively, are shown in Fig. 6.

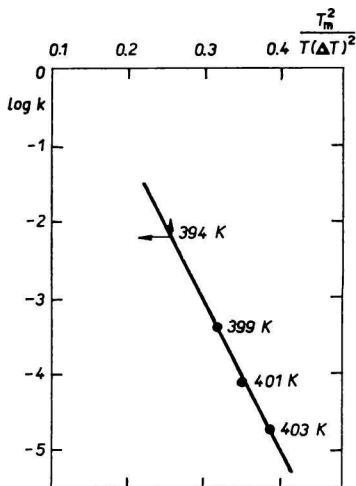


Fig. 4. Dependence of crystallization rate constant for crystalline polypropylene as a function of supercooling.

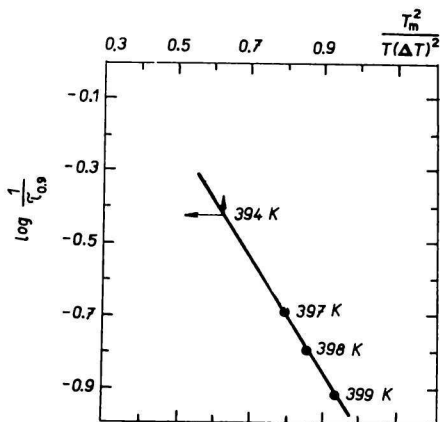


Fig. 5. Relation of  $\tau_{0.9}$  as a function of supercooling for polypropylene in the mixture with 2-hydroxybenzophenone.

*Microphotographic observation*

In Figs. 7–12 microphotographs of spherulites of pure crystalline polypropylene and its mixtures with chosen photostabilizers made between parallel polars can be seen.

**Discussion**

From the results shown in Table 1, it follows that similarly as in the case of alkoxy derivatives of 2-hydroxybenzophenone [1], compatibility of 2(2'-hydroxy-5-*n*-alkylphenyl)benzotriazoles with crystalline polypropylene is bettered along with the prolongation of the *n*-alkyl substituent. It is remarkable that also in this case the value of the heat of fusion of polymer depends on the kind of diluent that is at variance with Flory's assumption. Differences in the melting temperatures are, however, less expressive compared to the alkoxy derivatives of 2-hydroxybenzophenone [1]. These differences appeared to be connected with differences in the rate of isothermal crystallization.

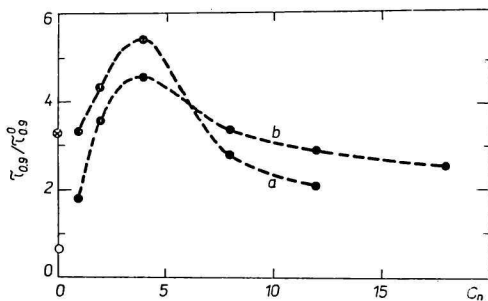


Fig. 6. Dependence of ratio  $\tau_{0.9} / \tau_{0.9}^0$  vs. number of carbon atoms in alkoxy and alkyl substituents of BPhC<sub>1-18</sub> and BPhC<sub>1-12</sub>.

a) PhBTC<sub>1-12</sub>; b) BPhC<sub>1-18</sub>.  
 ○ 2-HOPhBT; ● 2-HOBPh.

Table 2

Kinetic parameters of polypropylene crystallization in the presence of different photostabilizers

Sample	$n$	$k$ [ $\text{min}^{-1}$ ]	$\tau_{0.5}/\tau_{0.5}^0$	$\tau_{0.9}/\tau_{0.9}^0$
IPP	3.16	$8.6 \times 10^{-3}$	—	—
2-HOBPh + IPP	3.2	$4.6 \times 10^{-2}$	0.6	0.6
BPh + IPP	3.3	$1.9 \times 10^{-5}$	6.5	5.8
BPhC <sub>1</sub> + IPP	3.0	$1.6 \times 10^{-3}$	1.8	1.7
BPhC <sub>4</sub> + IPP	3.0	$8.4 \times 10^{-5}$	4.6	4.5
BPhC <sub>2</sub> + IPP	3.0	$1.9 \times 10^{-4}$	3.6	3.5
BPhC <sub>8</sub> + IPP	3.0	$2.1 \times 10^{-4}$	3.4	3.3
BPhC <sub>12</sub> + IPP	3.0	$3.4 \times 10^{-4}$	2.9	2.9
BPhC <sub>18</sub> + IPP	3.0	$5.6 \times 10^{-4}$	2.5	2.5
PhBTC <sub>1</sub> + IPP	3.0	$2.4 \times 10^{-4}$	3.4	3.3
PhBTC <sub>2</sub> + IPP	3.0	$1.1 \times 10^{-4}$	4.5	4.3
PhBTC <sub>4</sub> + IPP	3.0	$5.5 \times 10^{-5}$	5.6	5.4
PhBTC <sub>8</sub> + IPP	3.0	$4.2 \times 10^{-4}$	2.8	2.7
PhBTC <sub>12</sub> + IPP	3.0	$1.0 \times 10^{-3}$	2.1	2.0
2-HOPhBT + IPP	3.0	$2.6 \times 10^{-4}$	3.3	3.2

The course of dependences shown in Figs. 2 and 3 suggests a good agreement with relations (2) and (3). The values of Avrami exponent  $n$  (Table 2) show that the used polypropylene crystallizes in spherulite form from instantaneous nuclei ( $n = 3 + 0$ ). Nearly equal values of Avrami exponent enable us to compare the rate constants of crystallization of applied mixtures. From Table 2 and Fig. 6 it can be seen that mixtures of the first members of homological series of stabilizers with polypropylene (methoxy, ethoxy or methyl, ethyl) crystallize faster than those of butoxy or butyl derivatives. Further prolongation of alkoxy and alkyl substituents results in the gradual increase in the crystallization rates of the mixtures, but the obtained values are lower than those for pure isotactic polypropylene as can be seen in Fig. 6.

High values of the interaction energy of mixtures of these first members of stabilizers series with polypropylene suggest the poorest compatibility. Their behaviour in the

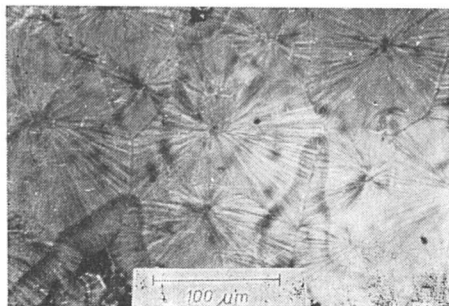
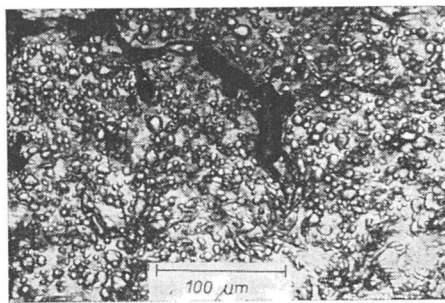
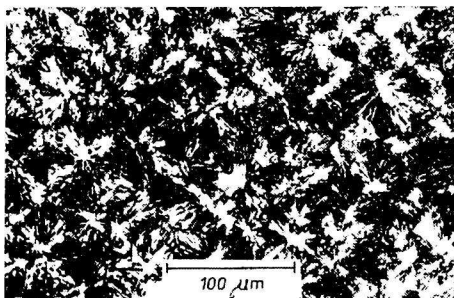
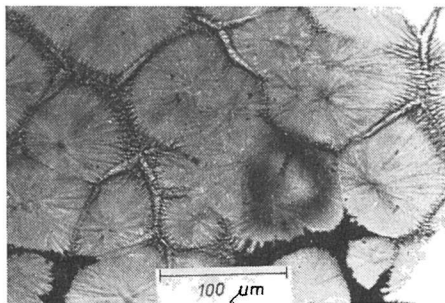


Fig. 7. Pure crystalline polypropylene.

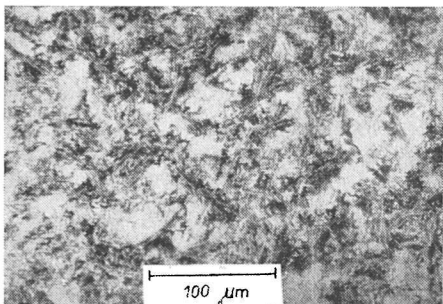
Fig. 8. Mixture of 20% (v/v) of BPhC<sub>1</sub> with crystalline polypropylene.



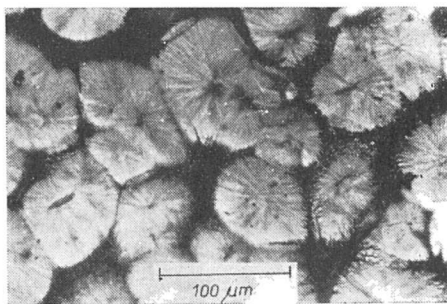
*Fig. 9.* Mixture of 20% (v/v) of BPhC<sub>2</sub> with crystalline polypropylene.



*Fig. 10.* Mixture of 20% (v/v) of BPhC<sub>3</sub> with crystalline polypropylene.



*Fig. 11.* Mixture of 20% (v/v) of PhBTC<sub>2</sub> with crystalline polypropylene.



*Fig. 12.* Mixture of 20% (v/v) of PhBTC<sub>4</sub> with crystalline polypropylene.

system can be compared with that of 2-hydroxybenzophenone (2-HOBPh) and 2(2'-hydroxyphenyl)benzotriazole (2-HOPhBT). We found that these compounds do not lower the melting point of polypropylene and are separated from the mixture. The obtained microphotographs confirm the results (Figs. 7–12).

The gradual increase in the crystallization rate of mixtures can be explained by the influence of paraffinic character of the stabilizers that results in their better adhesion and dispersion in polymer. When considering the fibrous structure of polypropylene spherulites we can assume a similar location of stabilizer molecules in this structure as in the case of low-molecular parts of polymer. The location of low-molecular weight substances in the fibrous area of spherulites results in the decrease of crystallization rate of polymer [5]. A photostabilizer with longer paraffinic substituent can be easier built in the fibrous area of polymer than that with the shorter substituent owing to its lower polarity and longer distance of polymer chain from the polar part of the stabilizer. This accounts for the lower retardation of polymer crystallization rate by higher members of homological series of the stabilizers.

The difference in the kinetic parameter values of the two series of stabilizers might be explained by different polarity of the basic compounds. Dipole moment of 2-HOPhBT is equal to zero [8] while that for 2-HOBPh is 2.71 D [9]. As can be seen from Table 2, crystallization rates pass through the minimum in dependence on number of carbon atoms paraffinic substituent.

This course is similar to that of  $\Delta H$  values. It is not so striking for phenylbenztriazole derivatives when compared to benzophenone derivatives where the minimum passes through the same derivative.

The influence of the ability of stabilizer to be built in spherulite fibrils of polymer is manifested by the crystallization rate of polypropylene in the mixture with benzophenone (BPh). The value of interaction energy density falls between BPhC<sub>1</sub> and BPhC<sub>4</sub>. The lower crystallization rate compared to BPhC<sub>4</sub> supports the assumption that the smaller is the ability of benzophenone molecules to be built in spherulite fibrils the greater is the decrease in the crystallization rate.

Discrepancy between our results and the assumption of *Parrini* and *Corrieri* [3] that the increase in compatibility leads to the crystallization rate decrease may be explained by the choice of the additives which are extreme from the point of view of their solubility in isotactic polypropylene (inorganic pigments, organic solvents).

*Cicchetti* and co-workers [6] have found that the diffusion rate of 2-hydroxy-4-*n*-alkoxybenzophenones in crystalline polypropylene decreases with the prolongation of *n*-alkoxy substituent that supports the results of this paper.

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