

Effect of Phase Transitions on the Volatility of UV Absorbers From Polypropylene

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SYNOPSIS

The volatility of 2-hydroxy-4-methoxybenzophenone and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole from isotactic polypropylene was studied by thermal methods in the temperature range that included the melting point of one of the stabilizers and the fusion of the polymer. The process proceeds according to the first order of kinetics. The rate constants of the stabilizers' volatility were calculated and the Arrhenius plots were constructed. The observed discontinuities in the Arrhenius dependences are interpreted as the result of the phase transitions of the polymer (melting) and the stabilizer. The activation energies for all zones were calculated. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Most synthetic and natural polymers are subject to chemical reactions because of the effect of the environment. The changes in physico-mechanical properties that include decrease in strength and elongation at break, changes in resistivity, colour changes, etc. are an external manifestation of these reactions. All these processes impair the useful properties of polymers, especially if the products are destined for long-term use.

Various types of additives are used to improve the useful properties and extend the service lifetime of polymers. Their role is to protect a polymer, to inhibit or to retard the degradation processes that proceed during an interaction of the heat, light, and oxygen with a polymer and in this way to extend the lifetime of the polymer products.

It has been suggested that the main factors that determine the effectiveness of stabilizers are¹⁻⁶:

1. The intrinsic stabilizer behaviour that is determined primarily by the chemical structure of the stabilizer. This behaviour may be

changed by transforming the active structural feature of the stabilizer.

2. Permanence of the stabilizer in the polymer. This factor includes solubility and/or compatibility of additives with polymers, volatility, and extractibility of stabilizers from polymers.

Except for these factors, we can also consider accessibility of the weak point in polymers by stabilizer molecules. This factor is important, especially in the case of the chain-breaking stabilizers (antioxidants, light stabilizers, quenchers of excited states, etc.), as in the case where a reaction proceeds between a degrading polymer and a stabilizer, and for polymeric or polymer-bonded stabilizers where the diffusion rate is very low.

For any particular stabilizer, its effectiveness is dependent on its concentration in the polymer. However, the concentration of stabilizers in polymers decreases during long-term use. The concentration changes of stabilizers in polymers may be a consequence of the two processes:

1. chemical reactions of stabilizers that are dependent on the structure and the stabilization mode of the stabilizer,⁷ and
2. physical loss of stabilizers from polymers.^{8,9}

The chemical loss of stabilizers is a consequence of the reactions of stabilizer molecules with active particles that arise during degradation processes caused by heat, light, and the presence of oxygen.⁷ The physical loss include the loss of stabilizers caused by physical processes. Here we can include volatility in the systems' solid phase-gaseous phase and liquid phase-gaseous phase, or extractibility of stabilizers in systems' solid phase-liquid phase. The summarization of the results obtained in the study of volatility and extractibility of stabilizers from polymers has been performed recently.^{8,9}

In spite of the fact that Matsumoto¹⁰ concluded that the state of the polymer, solid or molten, does not have a fundamental significance in the loss of antioxidant, the analysis of these losses showed that volatility of stabilizers can be especially influenced by phase changes of the system elements. In regard to the effect of the state of the polymer, Olson and Webb¹¹ have observed different degrees of the evaporative loss for a wide scale of UV absorbers below and above glass transition temperature in polycarbonate films. It has been also ascertained that the activation energy of the vapor pressure of various light stabilizers changes at the melting point of the particular stabilizer and is higher for solid phase than that for liquid phase.¹² It has been also observed recently^{13,14} that the rate of diffusion, the activation energy of diffusion, and solubility of different stabilizers changes at the melting point of the compound. Since diffusion is one of the steps that controls volatility of stabilizers from polymers,^{15,16} volatility of stabilizers ought to be changed at the phase transitions of the components.

In this work volatility of two UV absorbers of benzophenone and benzotriazole type from commercial polypropylene (PP) has been measured by thermoanalytical methods. The temperature range used for the measurements included a region of polypropylene fusion and melting point of the one of the stabilizers.

EXPERIMENTAL

Commercial unstabilized polypropylene Tatren (Slovnaft Bratislava, Czechoslovakia) of melting index 5.24 g/10 min was used. 2-Hydroxy-4-methoxybenzophenone (BP) and 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (BT) were used as light stabilizers. The mixture of PP with a stabilizer was homogenized in plastograph Brabender (Duisburg, Germany) for 5 min at 463 K and 60 rpm. The PP sheets with the thickness of 500 μm were pressed

for 5 min at 493 K and pressure 12.7 MPa, cooling 10 min. For the measurements discs of 3-mm diameter were cut from the sheet. The weight of the discs was ~ 4 mg.

The concentration of stabilizers was determined by UV spectroscopy with the Specord UV-Vis (Carl Zeiss, Jena, Germany). A sample of stabilized sheet was dissolved in hot toluene and after cooling the precipitated PP was filtered off. From the value of absorption of the filtrate, the concentration of the particular stabilizer was observed from the calibration plot. In the given concentration range the dependence of the stabilizer concentration on absorbance is governed by the Lambert-Beer law. For the determination of the BP content a 328 nm absorption band was used and for BT a 345 nm band was used.

Thermogravimetric measurements were performed with the thermobalance TGS-1 (Perkin Elmer). For the calibration, the calibration weights of the M class, tolerance of which is ± 0.005 mg for 1-50 mg were used, and for temperature calibration Alumel and Nickel were used. Thermal measurements were done by means of a differential scanning calorimeter DSC-1B (Perkin Elmer). The thermal calibration was performed according to known heat of fusion of indium and a set of the very pure chemicals Fischer Thermic Standards.¹⁷

RESULTS AND DISCUSSION

The analysis of the physical loss of stabilizers from polymers⁸ led us to the conclusion that the phase changes of stabilizers (melting point, boiling point) and polymers (glass transition, fusion) could influence the volatility of stabilizers from polymers. The measurements were performed in the temperature range that covered zone of fusion of the polymer and one of the stabilizers (BT), too. The experimentally used region for high temperatures was limited by the necessity to decrease the degradation processes to the smallest degree. In the range of low temperatures the measurements were limited by the used method. Since the measurements with regard to low concentration of stabilizers were performed at the maximal sensitivity of thermobalance, the extending of measurement time with lowering of temperature led to the oscillations of the records at small weight changes.

Though from the practical point of view the used stabilizers (BP, BT) are not suitable compounds for the stabilization of polyolefins with regard to the small length of the alkyl chain, their high volatility

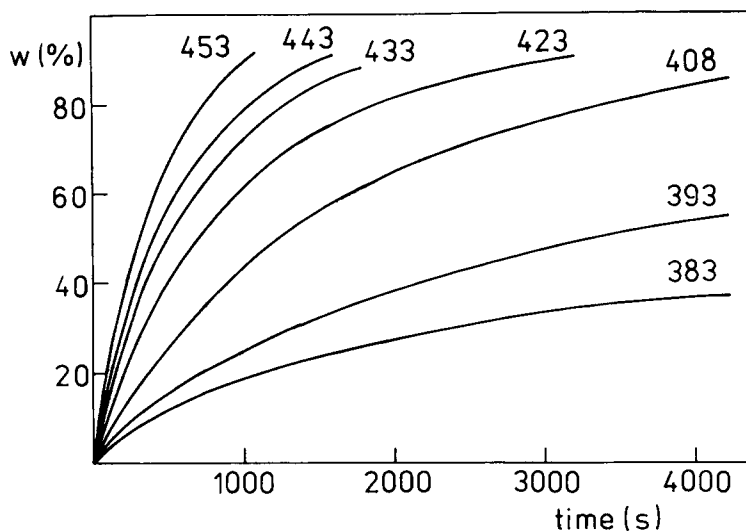


Figure 1 The time dependences of the volatility of 0.76 wt % of 2-hydroxy-4-methoxybenzophenone from isotactic polypropylene for different temperatures.

is preferable in comparison with the commercially used stabilizers with longer alkyl groups and therefore with increased compatibility with PP.^{8,12,18,19} Indeed, during the thermal compounding the drop from the initially intended concentration of 1 wt % to 0.76 wt % for BP and to 0.67 wt % for BT was observed. The possibility of easy and sensitive detection by means of absorption spectroscopy made them preferable compared with the other groups of stabilizers.

Volatility of stabilizers from PP was studied at concentrations near to the technological use by isothermal measurements of the weight decrease of a sample in nitrogen atmosphere. At the sample weight of ~ 4 mg, the total weight drop at the concentration of additive about 1 wt % represents about 0.04 mg. The control measurements have shown that in the temperature range and measurement times used the measurable weight change of the pure PP does not take place. Hence, oxidizing processes and with them connected releasing of gaseous products in the inert atmosphere does not interfere with the measurement of the stabilizer volatility. In other words, the weight decrease of the stabilized samples represents pure volatility process.

The development of the weight decrease of BP-stabilized PP sheet is illustrated in Figure 1, and similar courses have curves for volatility of BT from the PP sheets. It is evident from Figure 1 that in a relatively short measurement time, 15 min, the loss of BP is close to 90% for the highest temperature, and similar results were also obtained for the BT stabilizer. It is therefore clear that the thermal loss

is a pure physical process and it is not overlapped by chemical reactions of the stabilizers with the polymer matrix. From the data in Figure 1 it is also seen that the rate of stabilizer loss increases with the rise in temperature, and the curves have exponential character. Such development of volatility of stabilizers from polymers differs from the evaporation of the pure stabilizers where the dependence of the weight decrease on time is linear^{20,21} to what corresponds to the kinetic equation of the zero order. The exponential development of the curves of volatility of additives from polymers is already known,^{10,15,19,22} and is correlated by the first order kinetic equation.

According to Angert¹⁵ this dependence is described by analytical equation:

$$c/c_0 = 1 - \exp(-kt) \quad (1)$$

where c is the quantity of the substance evaporated in the time t , c_0 is initial concentration of the additive, and k is a rate constant of the process. Rearrangement of eq. (1) leads to the equation of a straight line:

$$-\ln(1 - c/c_0) = kt. \quad (2)$$

It follows from eqs. (1) and (2) that the rate of escaping of a stabilizer depends on the initial concentration of the stabilizer in the polymer. For our studies, the value of c_0 was determined by spectral analysis of the original samples. It has been ascer-

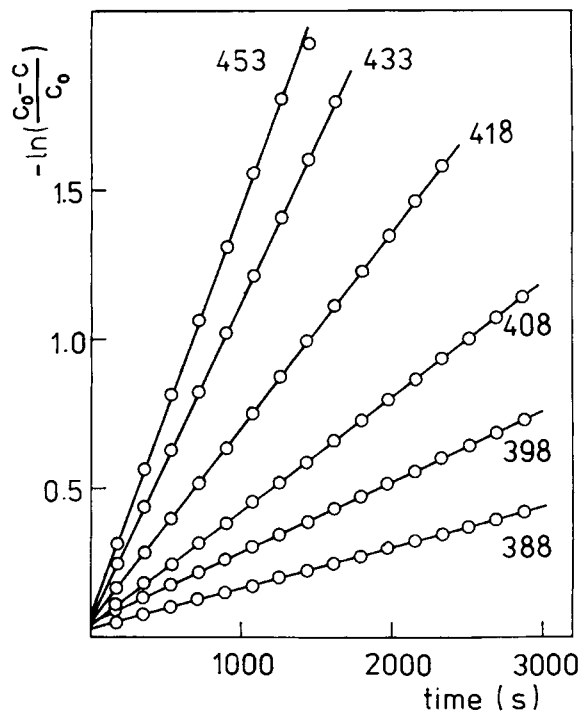


Figure 2 The first order dependences of the volatility of 0.67 wt % of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole from isotactic polypropylene for different temperatures.

tained that the content of stabilizers in sheets is constant and an average error of the determination is $\pm 5\%$. This fact can, however, cause relatively great errors in the calculation of the rate constants. Therefore, we tried to eliminate the influence of the initial concentration of the stabilizer on the value of rate constant by three- to fivefold parallel measurements under the same conditions.

Volatility of BT from PP in the sense of the eq. (2) is illustrated in Figure 2, and this function has similar development for benzophenone stabilizer as well. In the given coordinates the linear dependences were obtained from which the rate constants of volatility of stabilizers from PP were calculated as the slopes of the linear dependences in the temperature interval 383–458 K. The obtained results compare with the results of Durmis et al.¹⁹ who ascertained the values of rate constant $5.92 \times 10^{-4} \text{ s}^{-1}$ for BP at 393 K and $5.60 \times 10^{-4} \text{ s}^{-1}$ for BT. Our values are $2.44 \times 10^{-4} \text{ s}^{-1}$ for BP (extrapolated value), and $2.65 \times 10^{-4} \text{ s}^{-1}$ for BT which corresponds with Durmis' results. The differences in the values of the mantissa can be a result of the different degree of crystallinity of the polymer, and/or of the different concentration of stabilizers in the polymer.

The Arrhenius dependences of the rate constants of volatility on the temperature for 0.76 wt % of BP (average value) in PP are represented in Figure 3, and for 0.67 wt % of BT (average value) in Figure 4. From Figures 3 and 4, with the increase of temperature the slope of the dependence, $\ln k = f(1/T)$, changes. This abrupt change is in a contradiction with the results of Matsumoto¹⁰ that obtained the Arrhenius plot as a straight line above and below the melting range of the polymer. This break appears in the temperature interval between 423 and 433 K for both stabilizers, and for BT the first change appears already at 403 K. Let us mark the high temperature zone ($> 433 \text{ K}$) for both types of stabilizers as zone I, the region $< 433 \text{ K}$ as zone II, and the last part for BT stabilizer as zone III. The activation energies and preexponential factors of the volatility of both stabilizers from PP for the particular temperature ranges are given in Table I.

It follows from these data that activation energies of volatility of stabilizers are lower in the high temperature zone, and higher in the range of lower temperatures. Schmitt and Hirt¹² ascertained for various stabilizers that Arrhenius dependences of the vapour pressure of stabilizers on temperature have breaks at the melting points of pure stabilizers. The activation energies and preexponential factors have lower values for liquid phase than for the solid phase. Moisan^{13,14} has observed a similar effect for diffusion and solubility of different stabilizers in polyethylene. He ascertained a break in activation energies of diffusion at the melting points of some stabilizers, and a similar break in the solubility dependence on temperature. In our case, the temperature range include the melting point of BT (403 K). In the given temperature range of phase transition of BT, the change of activation energy really takes place, and the difference between the corresponding values represents 13.7 kJ/mol. This value is in a good agreement with the value of Schmitt and Hirt¹² that obtained the value 11.9 kJ/mol for the difference between the activation energies of vapour pressure in the solid and liquid phases for the same compound. Hence, the phase transitions of stabilizers influence their volatility from polymers.

The next break in the Arrhenius dependence appears for both stabilizers between 423 and 433 K that means in the range when both stabilizers are in liquid phase, we cannot expect their influence on the changes of activation energies. We can consider three possible effects that cause this break. All these effects could be connected with the phase transitions of semicrystalline polymers.

The semicrystalline polymers are characterized

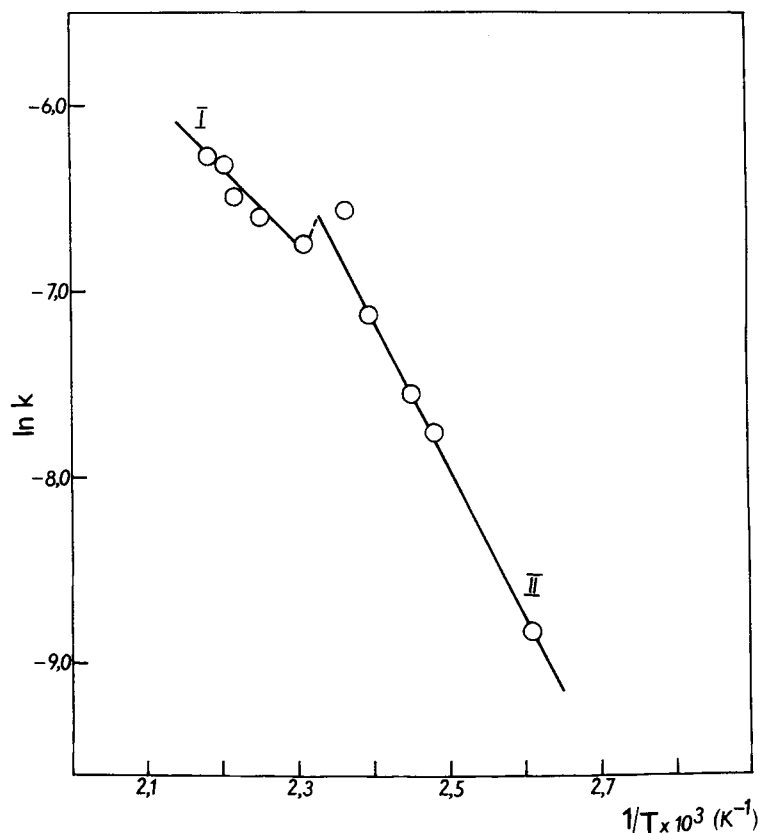


Figure 3 The Arrhenius plot of the volatility of 0.76 wt % of 2-hydroxy-4-methoxybenzophenone from isotactic polypropylene.

by the arrangement of atoms in elemental structural units, by the fraction of crystalline phase, by the size, shape, orientation, and aggregation of crystallites. Crystalline and semicrystalline polymers do not melt at exactly defined temperatures. Only annealing approaches the melting endotherms to some limited values. In the melting process of semicrystalline polymers, the amount of amorphous fraction increases until all crystallites are melted. The top of the endotherm of differential enthalpic curve (DEA curve) is considered to be the melting point. In this way determined the melting point of the pure isotactic PP is 443 K.²³ In Figure 5 is shown the DEA curve of the pure PP used in this work. It is seen that the beginning of the melting process is at 391 K and the melting point at the top of the endotherm is 436 K that means that it is lower than that of the pure isotactic PP. This difference is the result of the lower degree of crystallinity and the presence of an amorphous phase.

For both stabilizers, the temperature of the break in Arrhenius dependence is something lower than the melting point of the PP, 428 K for BP and 427

K for BT. With regard to the gradual processes of fusion and the presence of small amounts of additives that might be considered as plastifiers, we can, however, hold this temperature as a zone where an influence of the fusion of the polymer already appears. By the destruction of the crystalline lattice, a greater fraction of amorphous phase arises, the consequence of which is the concentration changes of stabilizers in the polymer matrix. It follows from Frank and Lehner's²⁴ and Calvert and Ryans'²⁵ results that during crystallization of semicrystalline polymers some kind of redistribution of additives in polymer matrix takes place. Stabilizers are rejected from the growing crystallites during cooling and accumulated in the amorphous phase between spherulites, in noncrystalline regions of spherulites, and in the defect spheres of the spherulites. A reversal process will therefore proceed during the fusion of the crystalline fraction of the polymer. Therefore, the first effect that would explain a break in Arrhenius plot could be the change of the stabilizer concentration in the polymer matrix. Because of the fusion of crystallites the amount of amorphous phase

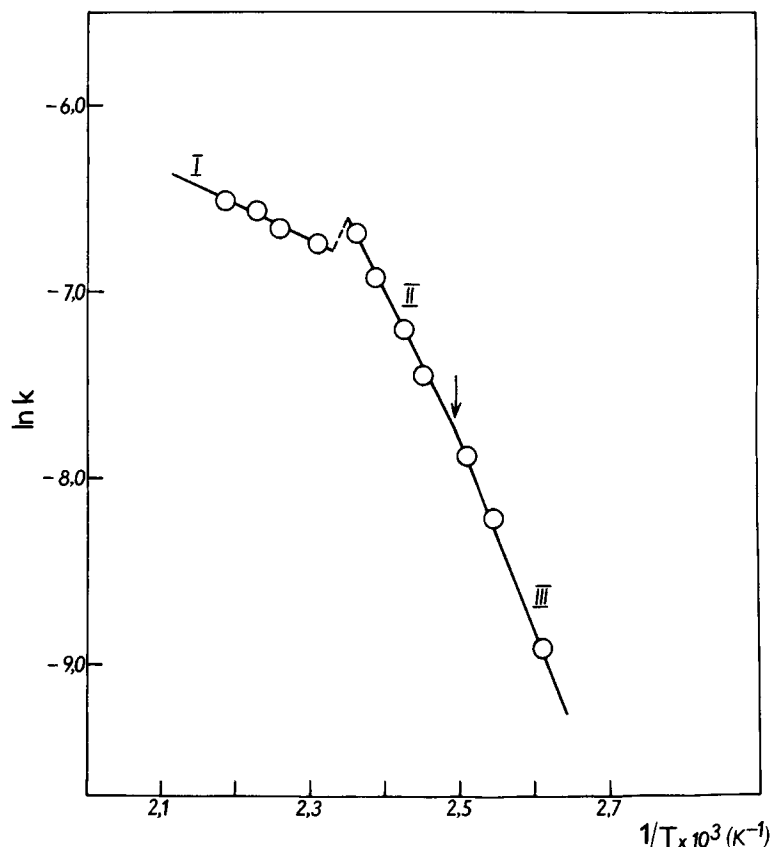


Figure 4 The Arrhenius plot of the volatility of 0.67 wt % of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole from isotactic polypropylene.

increases, and in this way a relative reduction of the stabilizer concentration in a bulk of polymer occurs. The relative decrease of the stabilizer concentration results in the decrease of concentration gradient that is the driving force of diffusion.

The rise of amorphous phase also decreases the fraction of crystallites. This means that the amount of obstacles that restrain diffusion of stabilizers in polymers decreases. For stereoblock PP for instance,

Cicchetti et al.²⁶ ascertained the activation energy of diffusion to be 50.7 kJ/mol for BP while in isotactic PP this value was 76.2 kJ/mol.²⁷ The mathematical relation of the dependence of diffusion coefficient on the volume of crystalline phase for diffusion of gases in polyethylene has been derived by Michaels and Parker,²⁸ and for PP it has been confirmed by Vieth and Wuerth.²⁹ The analytical expression of this dependence, eq. (3), includes an

Table I The Activation Energies and Preexponential Factors for the Volatility of 0.76 Wt % of BP and 0.67 Wt % of BT From Isotactic Polypropylene

Stabilizer	Zone					
	I		II		III	
	E_A (kJ/mol)	log A	E_A (kJ/mol)	log A	E_A (kJ/mol)	log A
BP	31.8	0.92	65.1	5.06	—	—
BT	15.4	1.07	73.0	6.14	86.7	7.98

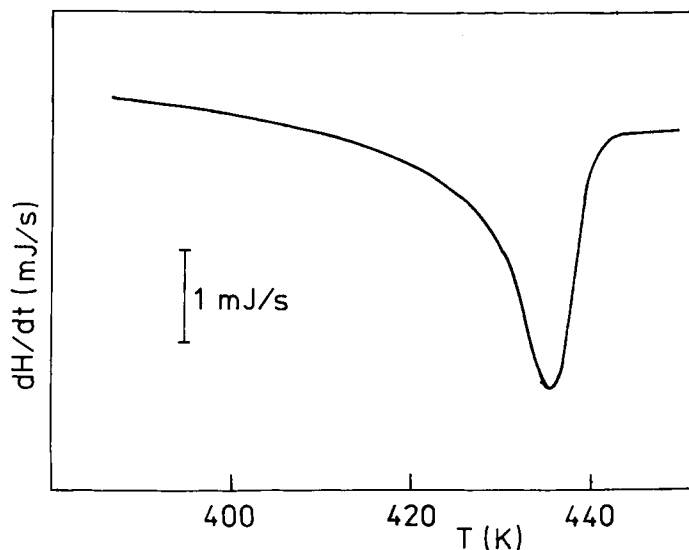


Figure 5 The differential enthalpic curve of the used isotactic polypropylene.

influence of the presence of crystalline phase in geometric impedance factor τ that contains a reduction of diffusion coefficient owing to the necessity of the molecules to bypass the crystallites and move through the amorphous regions.

$$D = D^*/\tau\beta \quad (3)$$

where D is diffusion coefficient, D^* is diffusion coefficient in completely amorphous polymer, and β is the chain immobilization factor. Also for diffusion of the great organic molecules, Klein³⁰ gives the dependence of diffusion coefficient on the morphology of polymer as an effect of the volume of the crystalline fraction. In the given temperature range and concentration of stabilizers, we can suppose¹⁶ that volatility is driven by diffusion of stabilizers to the surface of the polymer. Therefore, the above mentioned diffusion process will limit the volatility of stabilizers.

The last factor that could cause the changes of activation energy is the change of mobility of macromolecules with the increase of the temperature. In contrast to the diffusion of gases in polymers, diffusion of great organic molecules is more affected by the physical state of the polymer. While the size of already existing vacancies in polymers enables diffusion of gases because of their small dimensions, diffusion of great molecules is enabled by the segmental mobility of macromolecules. The segmental mobility of macromolecules is a thermally-activated process. The length of the segment necessary for effective diffusion process depends on the type of

polymer, and corresponds to about 20–30 carbon atoms.³¹ Therefore, the change of mobility of macromolecules and their segments at fusion of PP and with this connected creation of diffusion ways could be the next process that would explain breaks in Arrhenius dependences of volatility of stabilizers from PP.

This change is, however, most probably the reason of all three mentioned effects that take place at the melting of polymers. Simultaneously an effect of relative decrease of the concentration of stabilizer in the polymer, increasing of segmental mobility of the polymer chain, and also decrease of the physical barriers in diffusion ways because of polymer crystallites melting will become evident.

CONCLUSIONS

The study of the volatility of low molecular weight light stabilizers from isotactic polypropylene by thermal methods was performed. The escaping of the low molecular derivatives proceeds according to the first order kinetics.

The Arrhenius plots were constructed on the basis of the experimental rate constants. The breaks that appear in the Arrhenius dependencies were interpreted on the basis of the phase transitions of the stabilizer and polymer (fusion). The fusion of the polymer resulted in different concentration conditions as well as in changes in the diffusion process. The activation energies for all temperature zones were calculated.

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