

Thermal *cis*–*trans* Isomerization of 4-Diethylamino-4'-methoxyazobenzene in Poly(D(–)3-hydroxybutyrate) and Its Hydroxyvalerate Copolymer as a Probe for Characterizing Their Aging

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SYNOPSIS

The aging of bacterial polyester poly(D(–)3-hydroxybutyrate) has been studied by coloring it with 4-diethylamino-4'-methoxyazobenzene and determining the reduction in isomerization rate of the dye with aging, such a reduction being a measure of the loss in polymer sequential mobility that is responsible for the considered phenomenon. A preliminary test carried out on poly(ethylene terephthalate) colored with 4-diethylaminoazobenzene proved the isomerization of the dispersed dye to be a sound probe for determining the aging process. In the case of the bacterial polyester, the aging process appeared even above the polymer T_g value measured by calorimetric analysis. The kinetics and rate coefficients of aging were determined at 30°C for the examined polymers. Aging in the copolymer poly(hydroxybutyrate-hydroxyvalerate) was also investigated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The *cis*–*trans* isomerization of azo dyes, used to color polymers, is a useful probe for characterizing the morphological features of the polymer's amorphous phase. This technique has been confirmed by results from our previous work on polymer films of different morphology made of poly(ethylene terephthalate) (PET), isotactic polypropylene, polycaprolactam, poly(methyl methacrylate), and cellulose.^{1–7} As azo dyes some 4-diethylaminoazobenzenes and chryso-phenine were used.

Irradiation by visible light causes azo dyes to undergo *trans*–*cis* isomerization, after which the *cis* form reverts to the thermodynamically more stable *trans* form following a photochemical or thermal path.^{8–12} The kinetics of this return, when occurring in a polymeric medium, is strongly dependent on two closely intertwined factors: the free volume ex-

tent and the chain sequential mobility of the polymer. Thus, the *cis*–*trans* isomerization of azo dyes in a polymer under or around its glass-transition temperature (T_g) shows a deviation from the linear first-order kinetics normally observed above T_g , where the higher free volume extent and segmental mobility favor a simpler kinetics of the reaction, as happens in fluid media or in solution.

The more complex kinetics found under T_g can be adequately resolved^{1,2,4–7,13–15} as a multiplicity of simultaneous independent parallel first-order reactions, a multiplicity that resembles the unequal microenvironment and different free volume availability of the dispersed dye in the amorphous regions of the glassy matrix. Interestingly, there appear to be no significant kinetic modifications when the crystallinity of the sample is varied.

The ability of the considered isomerization to reveal changes in free volume extent and sequential mobility in a polymer could also be usefully applied to investigate the aging phenomena associated with loss in sequential mobility. The influence of polymer aging on the kinetics of *cis*–*trans* isomerization of

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azo dyes dispersed in a polymer was observed when studying polycaprolactam⁵ and polystyrene.¹⁶

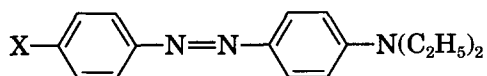
In this article the aging phenomena in bacterial poly(D(-)3-hydroxybutyrate) (PHB) and its hydroxyvalerate copolymer P(HB-co-HV) have been investigated, coloring them with 4-diethylamino-4'-methoxyazobenzene and studying the kinetics of its isomerization at different levels of aging. A preliminary testing of the reliability of the method has been carried out on PET below its T_g value.

The method, which is the subject of this work, represents a possible alternative to others reported in the literature. Effects due to the physical aging of polymers have been revealed in measurements of viscoelastic properties,^{17,18} fluorescence spectroscopy,¹⁹ impact testing,^{20,21} tensile testing,^{20,22} and differential scanning calorimetry (DSC).^{23,24} There has been a recent report of an approach²⁵ that demonstrates the aging of PHB by generating radicals in it by γ -radiolysis and following their decay with temperature, a measure of the increasing sequential mobility of PHB. To a certain extent, this approach is analogous to our proposed approach that follows the *cis-trans* isomerization of azo dyes used to color polymers.

EXPERIMENTAL

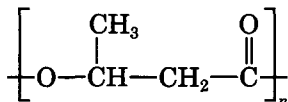
Materials

Azobenzenes (I) and (II) were kindly supplied by ACNA S.p.A.:

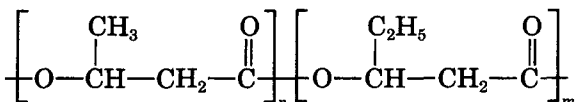


(I) X=H (C.I. number 11021, solvent yellow 56, reddish yellow) and (II) X=OCH₃ (not classified). They were purified by repeated crystallization from 1-butanol.

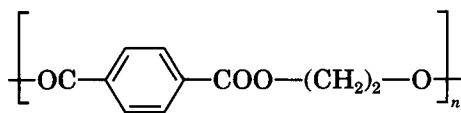
The polymers considered were:



PHB



P(HB-co-HV)



PET

The PHB ($M_w = 158,000$; $M_w/M_n = 2.85$) and P(HB-co-HV) ($M_w = 356,000$; $M_w/M_n = 2.72$; 6% HV) were kindly supplied by ICI as semicrystalline powders isolated from *Alcaligenes eutrophus* cultures. Their films (thickness 0.05 mm) were obtained by solution casting from tetrachloroethane at room temperature and drying under vacuum at 50°C for 24 h, annealing the samples. PET films ($M_w = 13,000$; thickness 0.04 mm) were obtained by extrusion at 280°C quenching in a cold air stream. The morphological characteristics of the polymer samples were as follows:

Polymer Sample	Specific Vol. (Vs, cm ³ g ⁻¹)	Crystallinity Index (β)	Glass-Transition Temperature ^a (T_g , °C)
PHB	0.8045	0.81	7
P(HB-co-HV)	0.8135	0.66	2
PET	0.7270	0.37	77

^a From DSC measurements.

Specific volume measurements were carried out at 25°C by flotation in toluene-carbon tetrachloride. The crystallinity index β was calculated assuming the following values of specific volume of amorphous (Vs, a) and crystalline (Vs, c) samples: 0.8518 (Vs, a) and 0.7937 (Vs, c) cm³ g⁻¹ for PHB²⁶; 0.8518 and 0.7942 cm³ g⁻¹ for P(HB-co-HV)²⁶; 0.7500 and 0.6870 cm³ g⁻¹ for PET.²⁷

Dyeing was carried out with 0.8–1.2% dyestuff calculated on the weight of the films. The process was started at 60°C, raising the temperature in 45 min to 125°C, and continuing at this temperature for 1 h. The dye concentration was chosen to have absorbance near 1 for isomerization measurements.

Measurements

For the kinetic measurements, the dyed polymer films were sandwiched between two quartz plates and irradiated with a 100-W tungsten lamp for 10 min, a time long enough to reach a photostationary state.¹¹ After irradiation the film was rapidly introduced into a Beckman DU7 spectrophotometer, in a thermostatted cell compartment maintained at the irradiation temperature. The change in absorbance at a wavelength corresponding to the absorption maximum of the *trans*-isomer gave the extent of the thermal return in a given time.

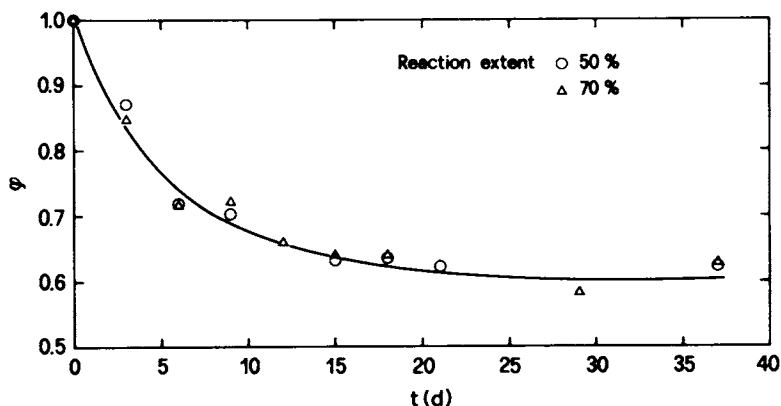


Figure 1 Aging process at 30°C of PET colored with dye (I) as revealed by the decrease with time of ϕ , the ratio between the *cis-trans* isomerization rate of the dye in the polymer sample and that in the annealed one, these rates being estimated at two levels of isomerization extent. Annealing conditions: 15 min at 100°C.

RESULTS

Derivatives (I) and (II) were used in dyeing the films of PET, PHB, and P(HB-co-HV) described in Experimental.

When polymers deaged by annealing were to be considered, the samples were thermally treated well above T_g prior to the kinetic measurements; this was to recover the equilibrium free volume and to erase any effect due to previous thermal histories. It must be noted that the dyeing process in itself gives deaged materials.

The annealed and variously aged dyed samples were subjected to irradiation and the thermal return

to the *trans* form of the dispersed dye was kinetically followed at constant temperature. The isomerization rate was found to regularly decrease with increase in aging time in all cases considered. In particular, when PET was investigated using dye (I) the trend depicted in Figure 1 was obtained, where term ϕ is reported vs. aging time. Such a term ϕ represents the ratio between the isomerization rate at a given aging time and that relative to the annealed sample (aging time = 0).

For polymers PHB and P(HB-co-HV) and dye (II), the trends shown in Figures 2 and 3 were obtained.

In Figures 1-3, two series of data are reported corresponding to two levels of reaction extent, namely 50 and 70%. The fair agreement of the two series of data can be appreciated.

In the case of PET, the sample was annealed at 100°C for 15 min and the aging was followed at 30.0

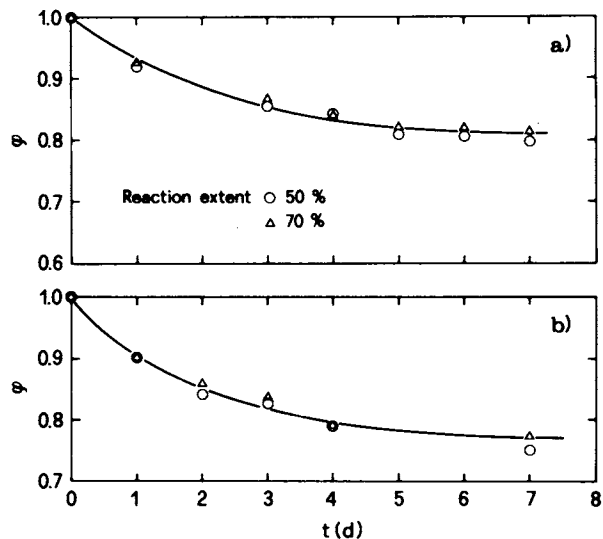


Figure 2 Aging process at 30°C of PHB colored with dye (II) evidenced as reported in Figure 1. Annealing conditions: (a) 30 min at 110°C; (b) 30 min at 50°C.

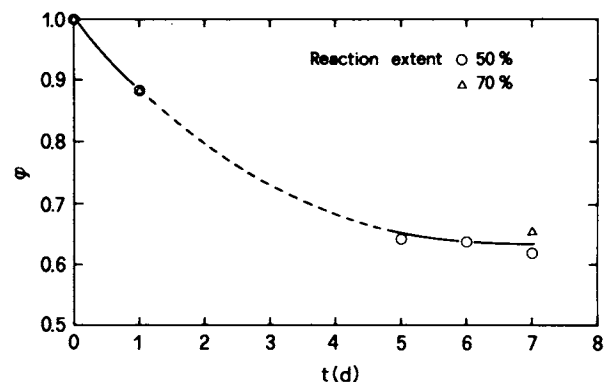


Figure 3 Aging process at 30°C of P(HB-co-HV) colored with dye (II) evidenced as reported in Figure 1. Annealing conditions: 30 min at 110°C.

$\pm 0.1^\circ\text{C}$ up to ca. 40 days. In the case of PHB, the sample was annealed at 110°C for 30 min in a first set of measurements [Fig. 2(a)], and at 50°C for 30 min in a second set [Fig. 2(b)]; in the case of P(HB-co-HV), only the deaging process at 110°C for 30 min was considered. The aging of PHB and P(HB-co-HV) was followed at $30.0 \pm 0.1^\circ\text{C}$ for up to 1 week.

At any given aging time, the *cis-trans* isomerization was kinetically studied at $30.0 \pm 0.1^\circ\text{C}$, measuring the absorbance of the samples at various times (up to 2 h). The reaction conversion (y), or reaction extent, was defined as:

$$y = \frac{\text{Abs}_t - \text{Abs}_0}{\text{Abs}_\infty - \text{Abs}_0} \quad (1)$$

where Abs_t , Abs_0 , and Abs_∞ are the absorbance values at time t , zero, and infinity (with reference to the *cis-trans* isomerization), respectively. When the completion of reaction was reached, the sample was allowed to age further.

Three time courses of the thermal return of the dye (II) dispersed in increasingly aged PHB are given as examples in Figure 4, and some values of half-life of such a reaction are reported in Table I for different polymers and dyes.

In the case of PHB, the *cis-trans* isomerization reaction on the deaged sample was investigated not only at 30°C but also at 25, 40, 50, and 60°C , in order to observe possible changes in the kinetic mechanism in this temperature range.

Table I Half-Lives of *cis-trans* Isomerization at 30°C of Dyes (I) and (II) Dispersed in Considered Polymers Variouslly Aged at 30°C

Polymer	Dye	Aging Time (days)	Half-Life of Isomerization (min)
PET	(I)	0	8.5
		6	11.8
		18	13.5
PHB	(II)	0	6.3
		5	8.0
P(HB-co-HV)	(II)	0	1.5
		5	2.5

DISCUSSION

The aging phenomenon is typical of polymers below T_g , due to the nonequilibrium nature of this state. When polymers are cooled to below T_g , the molecular mobility decreases significantly and the molecules become unable to reach the conformational structure and packing density needed for equilibrium at such temperatures. As the material tends to equilibrium there is a decrease in free volume excess with time; the rate at which this volume reduces governs the aging process, this rate being correlated with the chain segmental mobility in the amorphous phase of the polymer.

As polymers age their properties change in a way analogous to the changes that occur during cooling

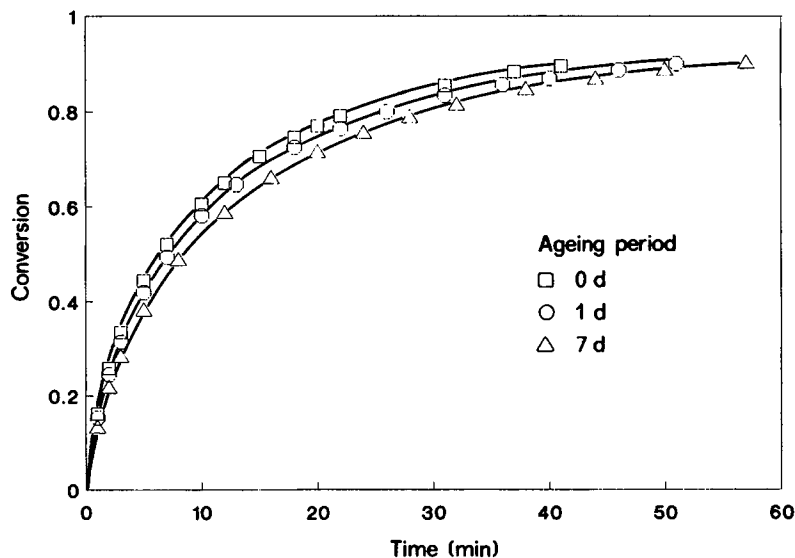


Figure 4 Time courses of the *cis-trans* isomerization at 30°C of dye (II) in PHB at different aging periods.

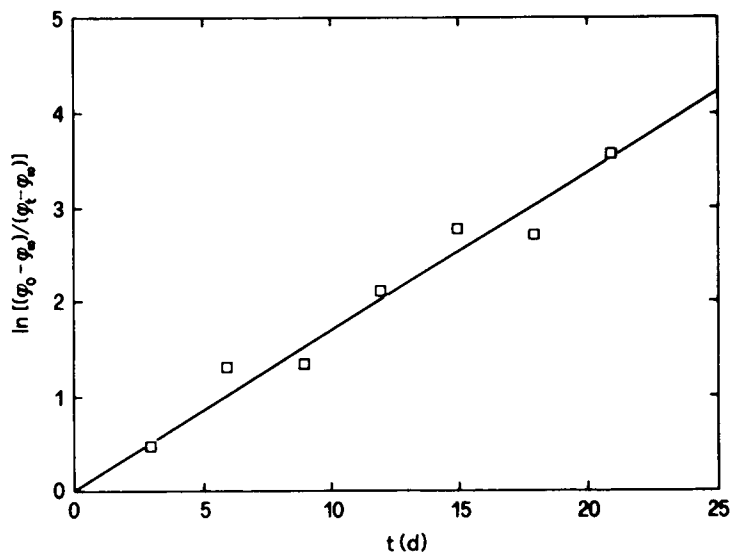


Figure 5 Aging at 30°C of PET interpreted as a first-order process (for terms φ_0 , φ_t , and φ_∞ , see text).

through T_g . The amorphous material becomes stiffer, more brittle, and its damping decreases, as do its creep and stress, relaxation rates, and dielectric constant. Aging reduces not only the free volume extent, but also the entropy and internal energy of the polymer, which therefore continuously loses heat, although in smaller and smaller amounts.

In principle, aging cannot occur at 0 K because the absence of molecular motions precludes any rearrangement, but when the temperature is raised to values at which vibrational motions can promote a structural mobility this phenomenon can take place, and its importance parallels the temperature increase. However, prior to reaching the T_g value of the polymer, namely in the glassy state, the rate of aging remains quite low because the molecular mobility only undergoes small enhancements, and hence the phenomenon can be easily observed. Conversely, at temperatures much higher than T_g , where conformational variations can occur easily, the thermodynamic equilibrium is fast established, ruling out any aging period. In other words, the chain mobility is so high to permit an instantaneous volume relaxation, making the properties of the material independent of its history.

The aging phenomenon in the case of PET at 30°C, i.e. under T_g , was revealed by the decrease in the rate of *cis-trans* isomerization of dye (I) dispersed in it (Fig. 1). Such a decrease is due to the decreasing chain segmental mobility that hampers the isomerization more and more with aging. The data in Figure 1 confirms that the reaction consid-

ered is a sound probe for aging investigations and allows an estimation of the aging kinetics.

The aging phenomenon can be interpreted as a single first-order process, characterized by the following integrated kinetic equation:

$$\ln \frac{\varphi_0 - \varphi_\infty}{\varphi_t - \varphi_\infty} = kt \quad (2)$$

where φ_0 , φ_t , and φ_∞ are the values of the term φ (the ratio between the isomerization rate of a given dye in the aged polymer sample and that in the annealed one) at time zero, t , and infinity (with reference to the aging process), respectively. As defined, $\varphi_0 = 1$, but φ_∞ can be experimentally estimated considering very long aging times.

Applying eq. (2) in a linear regression analysis on the data reported in Figure 1 for PET aging, after averaging them at the various considered times, gave a correlation coefficient $r = 0.99$ (Fig. 5), i.e., a value high enough to support the above assumption about the process kinetic order. A rate constant $k = 0.17 \pm 0.01 \text{ days}^{-1}$ was determined and, from this, a half-life of 4.1 days. The estimate of φ_∞ (0.61) revealed that the highest rate reduction of the probe reaction, corresponding to a very extended aging period, is 39%.

The aging observed in the case of PET was expected as it took place at 30°C, i.e. at a lower temperature than the T_g value of the polymer (77°C). On the other hand, interestingly, such a phenomenon was found to occur at 30°C also in the case of

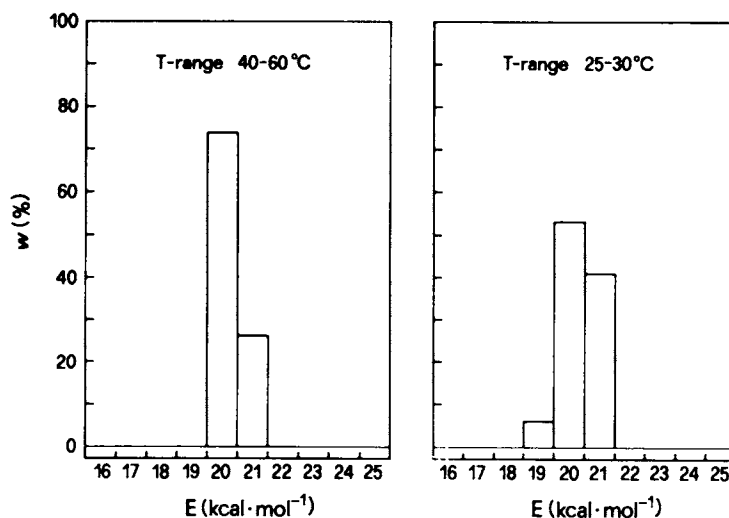


Figure 6 Spectra of the activation energies of the simultaneous independent first-order reactions involved in the *cis-trans* isomerization of dye (II) in polymer PHB in the two temperature ranges investigated (w is the relative importance of a single reaction).

polymer PHB (Fig. 2), for which $T_g \approx 7^\circ\text{C}$, as measured by calorimetric analysis. This can be explained only by accepting that, even at a temperature 23° higher than T_g , the chain mobility of PHB remains so scarce as to hamper the structural motions toward the equilibrium state, thus giving rise to an observable aging. Such a scarce chain mobility can be ascribed to the restrictions created by the numerous crystallites present in the considered semicrystalline PHB characterized by a high β value.

As mentioned earlier, the probe reaction employed here presents different kinetic behaviors depending on the nature of the polymer state. More precisely, on going from temperatures much higher than T_g to temperatures below T_g , an increasing complexity in the kinetic behavior can be observed, the limiting cases being a simple first-order reaction in the rubber state, and an extended multiplicity of simultaneous independent first-order reactions in the glassy state.

In the case of PHB, using a single first-order reaction model for the treatment of the experimental data obtained on the isomerization of dye (II) at various temperatures, the following values of the linear correlation coefficients (r) have been obtained:

$$0.997 (60^\circ\text{C}); \quad 0.995 (50^\circ\text{C}); \quad 0.995 (40^\circ\text{C}); \\ 0.985 (30^\circ\text{C}); \quad 0.985 (25^\circ\text{C}),$$

these values being referred to the same reaction extent, i.e. from the same Abs_0 value to the same final Abs_t value. It can be appreciated that on going from

40 to 30°C there is a significant lowering of r , that reveals that in this temperature interval the single first-order kinetic model becomes inadequate. In other words, between 40 and 30°C the microenvironment of the isomerizing dye varies, making the reaction pattern more complex. Reasonably, this change in the dye environment, consisting of the polymer matrix, can be attributed to a drop in its chain mobility.

The increasing kinetic complexity on going from higher ($40\text{--}60^\circ\text{C}$) to lower ($25\text{--}30^\circ\text{C}$) temperatures can also be revealed by adopting the more sophisticated kinetic approach previously reported.⁶ According to this, a more or less complex kinetic behavior of the considered isomerization in a given polymer, due to its more or less complex structural properties, results in a more or less spread spectrum of the activation energies that characterizes the multiplicity of reactions responsible for the process. A single frequency factor can be attributed to all these reactions on the acceptable assumption that the more complex structures affect only the energy barriers of the process.

In the framework of this sophisticated approach, the treatment of the data by an optimization procedure gives a frequency factor $A = 5 \times 10^{11} \text{ s}^{-1}$ and, for the two temperature ranges considered, the distributions of activation energies shown in Figure 6. It can be observed that at the higher temperatures a single reaction is prevailing; at the lower temperatures the spectrum becomes spread.

As a result, the probe considered reaction has been proved to reveal the limiting temperature at

which the slight chain mobility makes the occurrence of aging phenomena possible. In the case of PHB, this limiting temperature is in the range 30–40°C and represents an apparent T_g with regard to aging. It is significantly higher than T_g measured by calorimetry (7°C) as happens in the case of apparent T_g determined by thermodynamic mechanical analysis ($\approx 20^\circ\text{C}$).²⁸

The experimental data in Figure 2 on PHB aging at 30°C, treated as in the case of polymer PET by applying eq. (2), gave an aging rate constant $k = 0.52 \pm 0.03 \text{ days}^{-1}$ for an initial annealing for 30 min at 110°C, and $k = 0.58 \pm 0.05 \text{ days}^{-1}$ for an initial annealing for 30 min at 50°C. Taking into account their standard deviations the difference between the two k values does not appear significant. The corresponding half-life is of 1.2–1.3 days, and the highest reduction of the isomerization rate due to aging is between 19 and 23%.

In the case of copolymer P(HB-co-HV), the trend of φ vs. time was found to be somewhat irregular in the central zone of the process (dashed line in Fig. 3). Most likely the presence of two different units in the polymer matrix makes the kinetics of the isomerization reaction not very reproducible. In this case an estimate of k is 0.32 days^{-1} with a corresponding half-life of 1.8 days.

Interestingly, for copolymer P(HB-co-HV) the highest reduction in the isomerization rate due to aging (ca. 36%) appeared to be higher than that observed for PHB. Even the absolute isomerization rates for the copolymer were significantly higher, by a factor around 4 for each aging time.

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