Synthesis and Relaxation Properties of bis(5-Hydroxypenthyl)Phthalate - the Model Oligoester to Study the Relaxation Properties of Polyesters

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Summary: The description of polymer relaxation proprieties is the way to characterize the influence of polymer structure on its useful proprieties of stability and resistance. To perform physicochemical profiles of polymers the synthesis and investigation of model compounds was required. The instrumental methods such as NMR, FTIR, dielectric spectroscopy were used. The results of the experiments allowed us to improve the technology of the synthesis processes and the extension of the range of their usage. Moreover the obtained polymers were more stable and more resistant to degradation. To acquire the profile of the relaxation properties of the linear, hyperbranched and dendrite unsaturated polyester resins, the synthesis of the oligoesters as the model compounds was performed. Pentane-1,5-diol phthalic anhydride was used as substrate of the process. The structures of the obtained model compound were confirmed by elemental analysis and ^{1}H NMR and FTIR spectroscopy. Measurements of the relaxation processes of the model compound were also done. The determination of the α, β and β' relaxation processes for model oligoesters allow us to describe the practical properties of commercial compounds. The description of model relation of the relaxation process may facilitate the interpretation of the dependence between useful properties of polyesters and their molecular structure.

Keywords: bis(5-hydroxypenthyl)phthalate; dielectric spectroscopy; DMTA; FTIR; NMR; structural relaxation properties

Introduction

Continuous technological development leads researches to seek new solutions allowing for a wider usage of polyester resins. Studies on the synthesis and application of polyester plastics began in Poland at the Institute of Plastics in Warsaw[1] over 50 years ago. It is known that useful properties of products depend on the microstructure of the used polymers. Research of the polymer microstructure often requires syntheses of low-molecular model compounds. In the case of polyester these are suitable oligoesters.

Studies of a simple model system with the use of NMR and FTIR spectroscopy, calorimetric and thermo mechanical methods, allow us to determine the physicochemical properties of more complicated polymer systems.[2,3] Such research has made continuous improvement of the

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polyester production technology and the extension of their application possible.[4–7]

Considering the importance of polymer properties research with the use of model low-molecular compounds, we conducted the synthesis of bis(5-hydroxypenthyl) phthalate, as a fragment of polyester plastics, according to the generally accepted principles.[8–10] We chose this oligoester as the model compound to characterize the relaxation properties of unsaturated polyester linear resins and dendrite resins.[11] The possibility of the study of relaxation processes for oligoesters – suitable fragments of polyesters- allows for describing the relaxation processes of whole polyester molecule. However the synthesis of oligoesters of suitable structure is difficult.

Physicochemical characteristics of the obtained ester allowed us to study the relaxation processes of unsaturated polyester resin fragments. These studies may form the basis for determining the properties of polyester plastic relaxation and probably in the future enable us to find the reasons for the existing of property differences of useful linear, hyper branched and dendrite polyester plastics. The results of oligoester and linear polyester plastics relaxation measurements should make it possible to study the crosslinking processes of this type of polymers. Physicochemical properties of crosslinked polyester plastics depend both on chemical structures of unsaturated prepolymers and on crosslinked copolymer particle structure. Systematical investigation of oligoesters should lead us to the determination of their mutual relationships.[12]

The course of relaxation processes depends on compounds structure. It is known that temperature and pressure influences these processes. Measurement of relaxation times by the dielectric method can be conducted for particles in which the functional groups appear or the polarization of these particles occurs for some other reasons. Polyester plastics, suitable materials for relaxation research, enable us to determine the relation between their macromolecular structure and their useful properties. Impurities can deform results of dielectric studies. Consequently the research of well-defined model systems, with no impurities, should simplify the analysis of processes occurring in macromolecules and make drawing the right conclusions possible.[13,14]

Experimental Part

Phthalic anhydride (0,135 mol) and pentane-1,5-diol (0,27 mol) were used to synthesize bis(5-hydroxypentyl)phthalate. The mixture was heated with xylene until suitable quantities of water evaporated (0,135 mol = 2.4 cm^3) and then collected in an azeotropic receiver - the acid content was lower than 2–3 mg KOH/g. The obtained ester was then purified. The purification of ester was conducted in several stages. It consisted of repeated washing of substrates with water and acetone, the decolourization on active carbon, letting through a molecular sieve and drying under vacuum over anhydrous calcium chloride for one week under reduced pressure.

The elemental analysis was performed to find the content of carbon, hydrogen and oxygen in a 2 mg sample of obtained esters and oligoesters. The Automatic Elementary Analyzer (Perkin Elmer) was used to this goal.

The infrared spectra were recorded on Spectrum One spectrometer (Perkin Elmer), for film on KBr plates.

^{1}H NMR spectra were recorded on Ultra Shield 400 NMR spectrometer (Bruker) for the solutions of 20 mg sample in 1 ml of acetone-d_1. Hexamethyldisiloxane (HMDSO) was an internal standard for chemical shift determination.

The temperature-dependent dielectric measurements were carried out with Novo-Control GmbH equipment. We measured the complex permittivity over ten decades of frequency using an Alfa analyzer (10^{-2}–10^6 Hz), in combination with an Agilent network analyzer (10^7–10^9 Hz) in the temperature range 294 K to 328 K. The

temperature was controlled by the Quatro system, employing a liquid nitrogen-gas cryostat; temperature stability at the sample was higher than 0.1 K.

Results and Discussion

To confirm purity of the synthesized compound the ^{1}H NMR spectroscopy, the elemental analysis and the FTIR spectroscopy were used. Basing on the results of the NMR analysis the relative amount of protons for each proton group was assigned and compared with theoretical values based on the assumed structure. The theoretical number of aliphatic protons calculated form the assumed structural formula is in good agreement with the one calculated from integrated ^{1}H NMR spectra (Fig. 1). The results confirmed the assumed structure.

The results of elementary analysis are in good agreement with the ones calculated from the assumed compositions. The results confirmed that the products have the desired structure.

On the FTIR spectrum the intensive absorption band at 1742 cm^{-1}, originating from the stretching vibration of the ester group C=O, and two bands at 1580 cm^{-1} and 1599 cm^{-1} of the C–C bonds vibrations of aromatic ring were observed. The absorption band at 1760–1765 cm^{-1}, characteristic for the carboxyl group C=O was not observed. The bending vibration of the groups $–CH_2–$, –OH are also found in IR spectrum. This confirms the assumed structure of the synthesized compound.[15]

The studies of relaxation properties were performed on synthesized esters. The real ε' and imaginary ε'' components of dielectric permittivity were measured (Fig. 2). The measurements of the dielectric permittivity, dispersion and absorption were performed in the frequency range from 1^*10^{-2} to 1^*10^9 Hz.[16]

The application of the NOVOCONTROL software allows us to receive the spectrum immediately and elaborate it in the relation system of the imaginary component of the dielectric permeability ε'' versus frequency. Relaxation times of observed α, β and β'-relaxation processes (Table 1) were calculated from the received

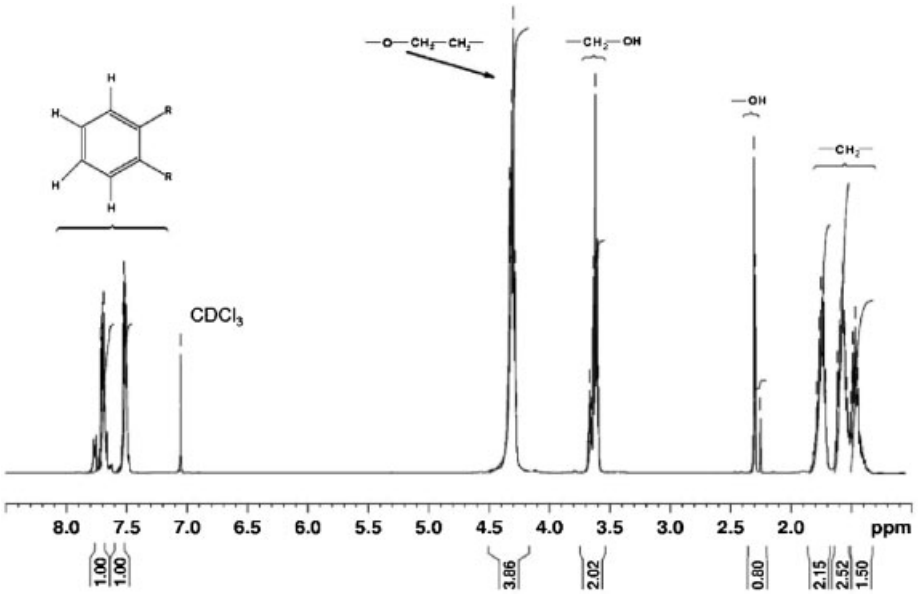

Figure 1.
^{1}H NMR spectrum of bis(5-hydroxypenthyl)phthalate.

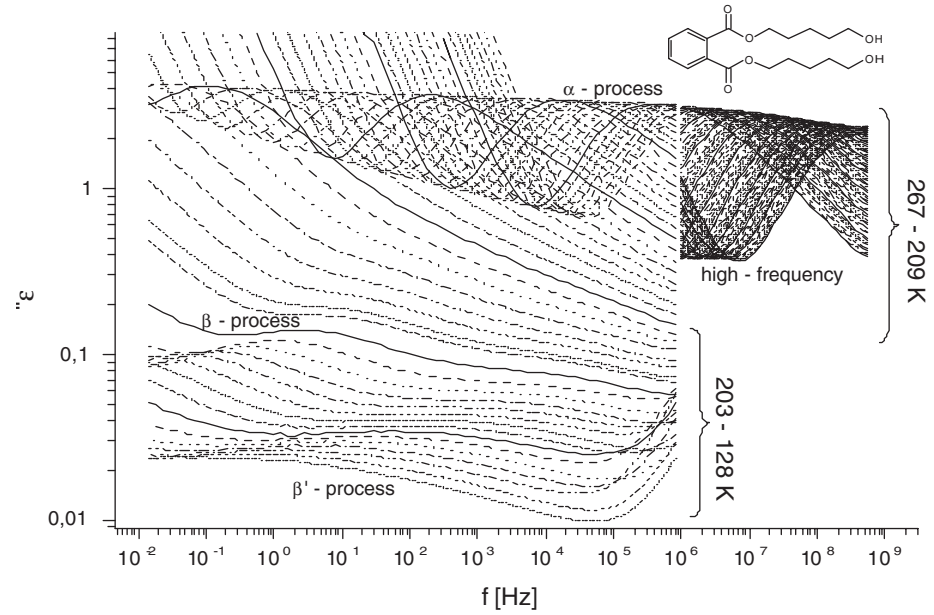

Figure 2.
The dependence of the imaginary component of dielectric permeability ε'' on the 5MBF oligoester frequency under the pressure 0, 1 MPa and at the variable temperature. 294K–128K. The process of α, β and β' relaxation.

spectrum by differentiation of dielectric losses ε'' (dielectric absorption). Coordinates of the point where derivative ε'' is equal to zero determine the relaxation time value.

$$\frac{d\varepsilon''}{d\log(f)} = 0 \qquad (1)$$

Processes of α and β' relaxations are comparable in respect of the relaxation times and are quicker than the β relaxation process. It was found that all determined relaxation times decrease with temperature increase. Observed processes of α relaxation are connected probably with movements of the whole molecule around neighboring one due to the small size of bis(5-hydroxypenthyl)phthalate. Processes of β relaxation are connected probably with the aliphatic chain rotation of the ester group. The relaxation process connected with the vibration of OH groups in molecule are observed in the dielectric spectrum. The change of the number of OH groups causes a reduction of intensity of the relaxation peaks and/or change of dipole moment that induces a shift of the relaxation processes to the higher frequency. The description of β' relaxation processes requires however further research of relaxation processes at constant temperature and under variable pressure, with an increase to about 20 GPa. This will probably allow us to ascribe it to movements of the relevant fragments of the investigated diester.

Table 1.
Relaxation time for observed processes of α, β and β' relaxation.

Process	Relaxation time [s]	Temperature range [K]
τ_α	$1{,}534 \cdot 10^{-7}$–3,835	267–209
τ_β	$4{,}71 \cdot 10^{-3}$–84,49	203–158
$\tau_{\beta'}$	$3{,}94 \cdot 10^{-6}$–$3{,}78 \cdot 10^{-1}$	203–128

Except for the highest measurement temperatures, the secondary peaks, although weak, are sufficiently isolated so that no deconvolution from the α peak is

necessary. The relaxation times for all three processes, defined from the peak maxima, are displayed in Fig. 3. Both secondary processes exhibit the Arrhenius behavior, with activation energies equal to 58.8 ± 1.3 and 32.6 ± 0.4 kJ/mol for τ_β and τ_γ, respectively. From the Arrhenius slope at $T_g = 204.7$ K value activation energies for (-processes gives 280 kJ/mol. The α relaxation process has a Vogel – Fulcher (VF) temperature dependence,

$$\log \tau_\alpha(T) = \log \tau_0 + \frac{B}{T - T_0} \quad (2)$$

with $\log \tau_0 = -12.97 \pm 0.01$, $B = 649 \pm 3$ K, and $T_0 = 161.3 \pm 0.1$ K. Extrapolation to $\tau_\alpha = 100$ s gives 204.7 K for the glass transition temperature T_g.

In the non-linear Vogel-Fulcher (VF) dependences as for relaxation process α, the modified Vogel-Fulcher-Tamman function (VFT) can be applied [16] for determination of the fragility of the materials:

$$\tau = \tau_\infty \exp^{\left(\frac{D_T \bullet T_0}{T - T_0}\right)} \quad (3)$$

where τ is the relaxation time [s]; τ_∞ is time constant for oligomers (10^{-13}s); T and T_0 are temperature of measurement and temperature of ideal phase transition ($\geq T_g$ K), respectively; D_T is a non-dimensional parameter describing flexibility or fragility of glass-like materials.

For the hard materials parameter D_T is small ($D_T \leq 10$).

D_T value can be determined from the Equation (4):

$$D_T = T_0 + [(\ln \tau - \ln \tau_\infty) * (T - T_0)] \quad (4)$$

The existence of two relaxation processes β and β′ in the same temperature range is not clear. The relaxation process β′ occurs probably as a result of the formation of hydrogen bonds between some of the molecules. We are in the course of study

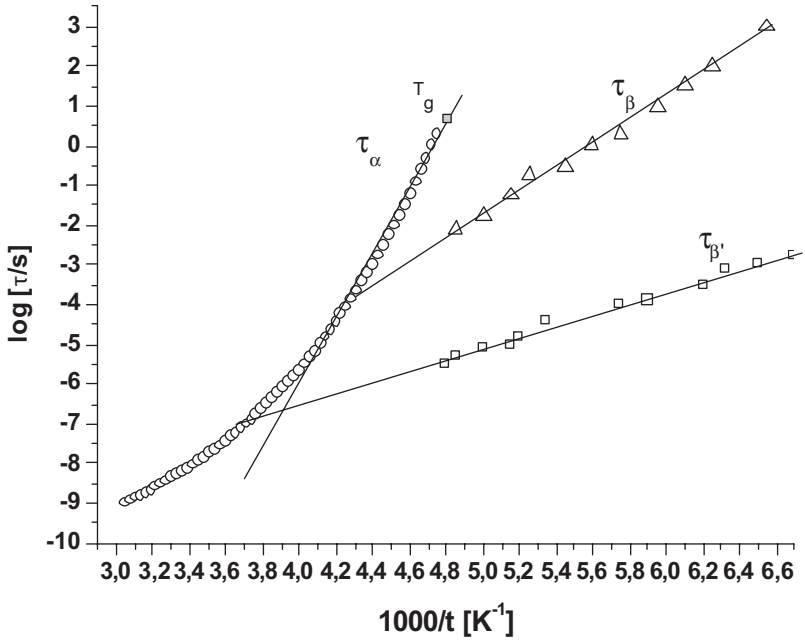

Figure 3.
Arrhenius plot of the relaxation times for the α (○), β (△), and β'(□) processes. The solid lines are the fit of Eq. (1) to τ_α and linear fits (Arrhenius behavior) to the secondary relaxations, yielding $E_\beta = 58.8 \pm 1.3$ kJ/mol and $E_{\beta'} = 32.6 \pm 0.4$ kJ/mol. Extrapolations of the latter yield the intersections with τ_α at apparent merging temperatures, $T_{\alpha\beta} = 233.2$ and $T_{\alpha\beta'} = 281.6$ K.

of bis(5-hydroxypenthyl)phthalate homologues in order to explain this phenomenon.

Conclusion

The results of IR, ^{1}H NMR and elemental analysis confirm the structure and high purity of synthesized bis(5-hydroxypenthyl)phthalate.

The relaxation studies of obtained bis(5-hydroxypenthyl)phthalate were performed by means of dielectric spectroscopy. The presence of β'- relaxation processes, apart from the α and β relaxation ones, were found.

To draw more detailed conclusions further experiment should be performed with the use of the Dynamic Mechanical Thermal Analysis (DMTA). The particular atoms and groups affect the mechanical relaxation as well as the dielectric one. The Dynamic Mechanical Thermal Analysis enables the study of dependence of characteristic processes connected with dynamic behavior of chain or chains systems e.g. local movements, vibration or relaxation transition on temperature. DMTA technique allows us to determine the relations between macromolecular parameters and molecular structure of polymer. However, in mechanical study, contrary to dielectric one, the Young's modulus can be determined, since it depends not only on the kind and size of monomeric unit but also on the way of its location with relation to other ones in entire chain of polymer. In the mechanical study dipole moment is neglected. Therefore DMTA technique can be useful for determination of relaxation processes in non-polar molecules or in molecules with small dipole moment This technique complements the results obtained from dielectric spectroscopy.[18,19]

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[1] P. Penczek, Z. Kłosowska-Wołkowicz, *Polimery*, **1997**, *42*, 294–297. (in polish)
[2] S. J. Evans, P. J. Haines, G. A. Skinner, *Termochim. Acta*, **1996**, *278*, 77–83.
[3] S. H. Mansour, N. Ikladious, *Polymer Testing*, **2002**, *21*, 497–505.
[4] R. Sengwa, S.C. Chaudhary, *Polymer*, **2002**, *43*, 1467–1471.
[5] A. Burgath, A. Sunder, H. Frey, *Macromol. Chem. Phys.* **2000**, *201*, 782–791.
[6] K. Ishizu, D. Takahashi, *Polymer*, **2000**, *41*, 6081–6086.
[7] N. Charles, Moorefield, G. Newkome, *Adv. Dendritic Macromol.* **1994**, *1*, 1–67.
[8] U. Edlund, C. Albertsson, *Adv. Drug Deliver. Rev.* **2003**, *55*, 585–609.
[9] K. Nalampang, A. Jonson, *Polymer*, **2003**, *44*, 6103–6109.
[10] C. Diakoumakos, F. Jones, *Polymer*, **2001**, *42*, 2277–2288.
[11] M. Paluch, M. Sekuła, S. Maślanka, K. Mańczyk, W. W. Sułkowski, S. Rzoska, J. Zioło, *J. Chem. Phys.* **2004**, *120*, 2020–2025.
[12] G. Gündüz, *Polymeric Materials Encyclopedia* Vol *11*, CRC Press, Now York, **1996**
[13] L. Mangeng, M. Shim, K. Sangwook, *Europen Polymer Jur.* **2001**, *37*, 1075–1078.
[14] E. Malmstrom, A. Hult, *Polymer*, **1997**, *38*, 4873–4879.
[15] B. Schrader, Raman – IR. Atlas of Organoc Compounds, VCH – Ver – Ges, Weinheim, **1989**.
[16] P. Hedvig, Dielectric Spectroscopy of Polimers, Akademiai Kiado, Budapest, **1977**.
[17] S. Maslanka, M. Paluch, W.W. Sulkowski, *J. Chem. Phys.* **2005**, *122*, 084511.
[18] A. Danch, W. Osoba, *J. Therm. Anal. Cal.* **2003**, *72*, 641–650.
[19] I. M. Ward, Mechaniczne właściwości polimerów jako tworzyw konstrukcyjnych., PWN, Warszawa, **1975**.

