# The Model Oligoester Bis-(2-Hydroxypropyl)phthalate - Synthesis and Relaxation Properties

*Wiesław W. Sułkowski,*[*1] Sławomir Maślanka,[1] Danuta Pentak,[1]
Agnieszka Wolińska,[1] Henryk Janeczek,[2] Marian Paluch,[3] Adam Danch,[3]
Anna Sułkowska[4]*

**Summary:** The study of polymer properties requires the synthesis and analysis of simple model compounds. In this work the suitable oligoesters were used for this purpose. The investigation of model oligoesters allows us to describe the physicochemical and utility properties i.e. stability and resistance of linear, branched and dendrite polyesters. To achieve this aim the model oligoesters were synthesized and their physicochemical properties were described. The structure of the oligoesters was confirmed with the use of NMR, FTIR spectroscopy and elemental analysis. A detailed study of the relaxation properties using broadband dielectric spectroscopy and Dynamic Mechanical Thermal Analysis (DMTA) was also performed. A description of the $\alpha$ relaxation process and different dielectric and DMTA $\beta$-relaxation processes for the oligoesters are indispensable to determine the relaxation properties of the suitable polyesters.

**Keywords:** bis-(2-hydroxypropyl)phthalate; dielectric spectroscopy; DMTA; FTIR; NMR; structural relaxation

## Introduction

Over the last five decades continuous interest in polyesters has been observed.[1] The development of technological and analytical possibilities has driven scientists to serek new applications for obtained unsaturated polyesters. Hyperbranched and dendrite unsaturated polyesters are used to obtaine alkyd resins for painting materials with lower solvent contents.[2–4] However it was noticed that cross-linked polymer materials after some weeks exhibited undesirable properties e.g. the subsurface stains and the hardness of the materials surface decreases. These changes probably take place due to the cross-linked polymer structure. The study of the polymer microstructure requires the synthesis of simple model systems. Oligoesters are suitable model compounds for polyesters. The study of model oligoesters make it possible to describe the physicochemical and utility properties of more complicated systems such as cross-linked polymers with the use of NMR, dielectric and mechanical spectroscopy, calorimetric and thermogravimetric analysis etc.[5,6]

The course of the relaxation processes of the polymeric materials depends on the structure of the macromolecules. However pressure and temperature also affect this processes. The determination of the relaxation times of polymers using dielectric methods is possible only for molecules with polar functional groups. Polyesters are that kind of molecules. A description of the

---

[1] Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland
E-mail: wsulkows@uranos.cto.us.edu.pl
[2] Centre of Polymer Chemistry, Polish Academy of Science, M. Curie-Skłodowska 34, 41-800 Zabrze, Poland
[3] Institute of Physics, University of Silesia, Uniwesytecka 4, 40-007 Katowice, Poland
[4] Department of Physical Pharmacy, Medical University School, Jagiellońska 4, 41-200 Sosnowiec, Poland

structure of the model compounds and the knowledge of their relaxation properties allows us to simplify the interpretation of the correlations between the properties of polyester macromolecules and the utility properties of polyesters materials. The description of these dependences for the linear macromolecules is essential for future investigation of cross-linked processes of unsaturated polyesters.[7–9]

Dynamic mechanical thermal analysis (DMTA) belongs to one of the most frequently used methods for characterizing thermal, viscoelastic and structural properties of polymeric materials. The possibility of assessing the temperature- and time-dependent behavior, the extent of phase mixing in blends, the degree of crosslinking, crystallinity, interfacial adhesion, ageing and degradation make this technique extremely valuable in the process of testing and designing new materials.[10] Nowadays the macroscopic properties of polymers and other complex materials are mainly interpreted on the basis of the underlying microscopic phenomena. Particularly, focusing on the temperature dependence of the average relaxation time may lead to predicting molecular mobility and to fine tuning of the final properties.[11]

### Materials and Methodology

Phthalic anhydride (0.135 mol) and propane-1,2-diol (0.270 mol) were used to synthesize bis-(2-hydroxypropyl)phthalate. The mixture was heated with xylene until the suitable quantities of water evaporated (0.135 mol = 2.4 $cm^3$) and then collected in an azeotropic receiver.[12] 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 of 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 determine the content of carbon, hydrogen and oxygen in 2 mg sample of obtained esters and oligoesters. The Automatic Elementary Analyzer CHNS-O (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 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 complex dielectric permittivity was determined in the frequency range from $1 \times 10^{-2}$ to $1 \times 10^{7}$ using the High Resolution Dielectric Analyser Alpha in the temperature range from 320 K to 220 K. In lower temperatures, liquid nitrogen was used for temperature stabilization.

The DMTA were recorded on analyser Q800 DMA (TA Instruments). Samples were spread on the glass silk type in the temperature range 313 K to 318 K, then samples were kept at ambient temperature 293 K to cool. Glass silk type with sample 4 cm in length, 1.5 cm in width and 0.25 cm in thickness was put into DUAL CANTILEVER measuring head of DMA. Measurements were conducted by two techniques: (1) dynamics i.e. to measure parameters with constant change of temperature in the range from 123 K to 333 K with heat rate 2 K/min; (2) isothermal i.e. with discrete change of temperature in the range from 223 K to 333 K. The former technique was used for fast testing of the sample at all chosen frequencies. The latter one allows for precise investigation of the relaxation region with wide range of frequencies from 0.01 to 200 Hz.

## Results and Discussion

The $^1$H NMR spectroscopy, the elemental analysis and the FTIR spectroscopy were used to confirm the purity of synthesized bis-(2-hydroxypropyl)phthalate. Basing on the results of the NMR analysis the relative amount of protons for each group were assigned and compared with theoretical values obtained for the predicted structure.

The theoretical number of aliphatic protons calculated form predicted structural formula are in good agreement with the one calculated from the integrated $^1$H NMR spectra (Fig. 1).

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

In the FTIR spectrum the intensive absorption band at 1745 $cm^{-1}$ originating from the stretching vibration of the ester group C=O, two bands at 1584 $cm^{-1}$ and 1600 $cm^{-1}$ of the C–C bonds vibrations of aromatic ring were observed. The absorption band at about 1760 $cm^{-1}$, characteristic for the carboxyl group C=O was not observed. The bending vibration of the groups $-CH_2-$, $-CH_3$, –OH and the stretching vibrations of the group –CH are also found in IR spectrum. This confirms the assumed structure of the synthesized compound.[13]

The studies of relaxation properties were performed on synthesized esters. The real $\varepsilon'$ and imaginary $\varepsilon''$ (Fig. 2) components of dielectric permittivity were measured.[14] The measurements of the dielectric permittivity, dispersion and absorption were performed in the frequency range from $1 \times 10^{-2}$ to $1 \times 10^{7}$ Hz.

These requirements for DMTA measurements were necessary to determine the characteristic relaxation times of the compound relaxation. The measurements were performed for bis(2-hydroxypropyl)phthalate. The $\beta$-relaxation process was observed on the basis of the results obtained with dielectric spectroscopy for bis(2-hydroxypropyl) phthalate d (Fig. 2). The rotation of the aliphatic glycol chain of ester group or the vibration of the carboxyl group around the polarization axis probably causes the observed process of $\beta$-relaxation. Relaxation time $\tau_\beta$ for the observed process was $2.45 \cdot 10^{-6} - 2.94$ [s] in the temperature range from 220 K to 320 K.

The results of DMTA study of bis(2-hydroxypropyl)phthalate showed the presence of two relaxation processes $\alpha$ and $\beta$ (Fig. 3). The $\alpha$-relaxation process is probably connected with the structural interactions between molecules while the $\beta$-relaxation process with the rotation of aliphatic glycol chains in diester of phthalic acid.[15]

For the relaxation processes observed with the use of DMTA and dielectrical spectrometry methods the dependences of

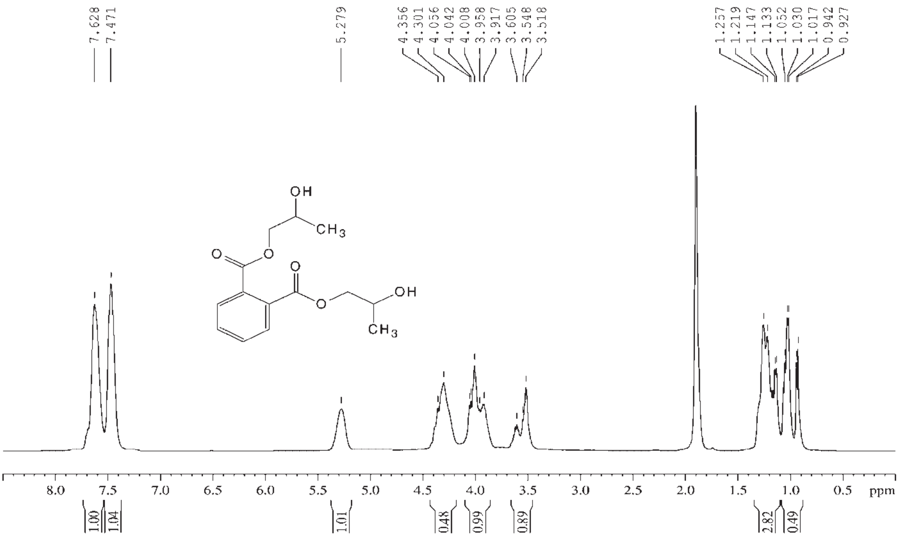

**Figure 1.**
$^1$H NMR spectrum of bis(2-hydroxypropyl)phthalate.

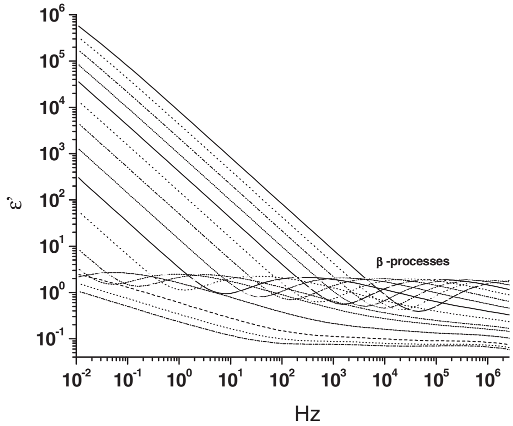

***Figure 2.***
Loss dielectric spectra of bis-(2-hydroxypropyl)phthalate at 0.1 MPa pressure and temperature range from 220 K to 320 K.

log ($f_{\max}$) as a function of reverse temperature (Fig. 4) was determined. The results showed that the $\alpha$-process is not an Arrhenius process while $\beta$-processes observed in both DMTA and dielectrical spectrometry are Arrhenius processes. Their activation enthalpy $H_A$ was determined.

The slopes of these linear fits obey the relation [16]:

$$\log f_{\max} = \frac{A - H_A}{(2.303 R T_{\max})} \qquad (1)$$

where: $R$ – gas constant

$H_A$ – activation enthalpy of the simple phase.

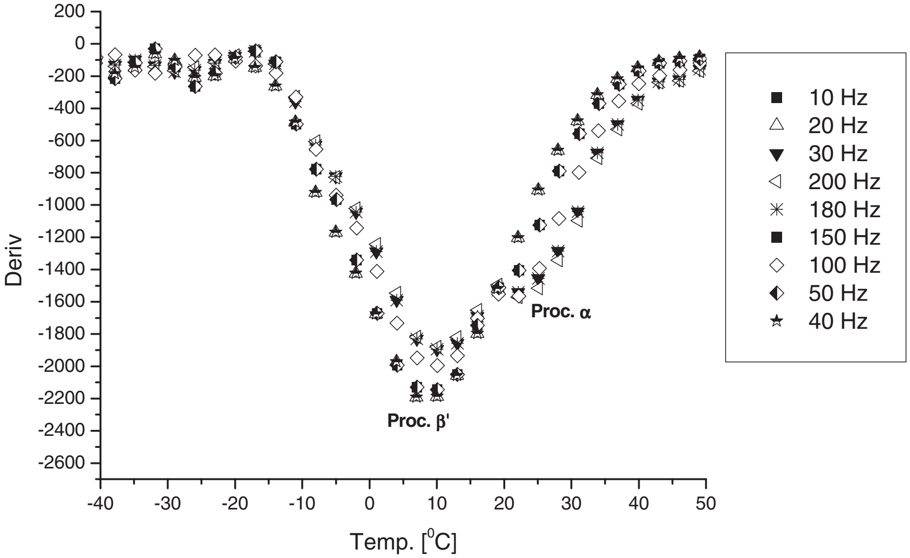

***Figure 3.***
Loss tangent (tgδ) derivative as a function of temperature for chosen frequencies for bis-(2-hydroxypropyl)phthalate from DMTA measurements.

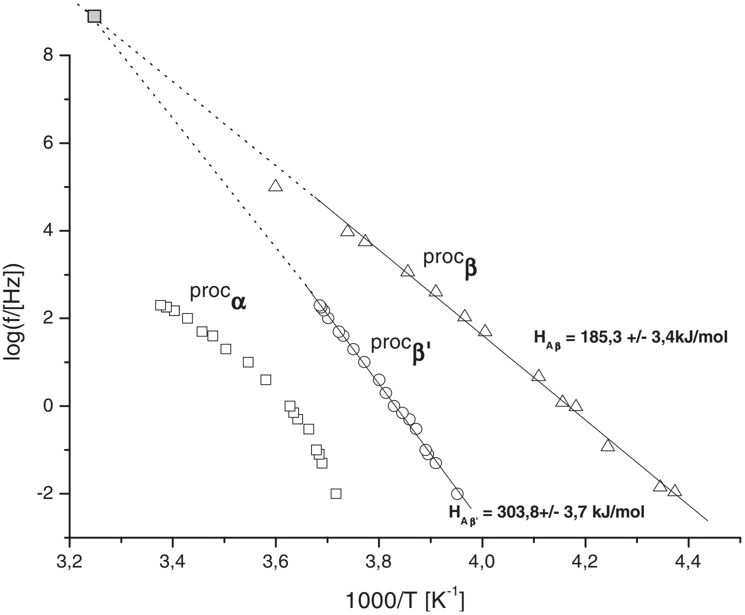

***Figure 4.***
Arrhenius plots for the structural relaxations of bis-(2-hydroxypropyl)phthalate for $\alpha$ (□) and $\beta$ (○) - processes (results of DMTA study) and $\beta$ (△) – process (results of dielectric spectroscopy study) and calculated activations enthalpy $H_A$ of $\beta$-processes.

The activation enthalpy data of the structural relaxation $\beta$-processes determined by two methods, i.e. the dielectric spectroscopy ($H_A = 185{,}3 \pm 3{,}4$ kJ/mol) and the DMTA ($H_A = 303{,}8 \pm 3{,}7$ kJ/mol), differ from each other. The reason of this difference can be explained by the fact that it is technically impossible to maintain the same conditions in both experiments. One of these technical problems which avoided, is the difference of the samples thickness. In dielectric spectroscopy measurements the sample is spread on capacitor plates and in DMTA measurements the sample is spread on a glass silk type. Moreover the cooling systems in both instruments vary and slight difference in the cooling and heating rates of samples occur during the measurements.

## Conclusion

The results of elemental analysis, infrared spectra and NMR spectra confirmed that the synthesized and purified bis-(2-hydroxypropyl) phthalate has the desired structure and purity.

The relaxation studies with dielectric spectroscopy and Dynamic Mechanical Thermal Analysis (DMTA) were performed for bis(2-hydroxypropyl)phthalate and activation enthalpy of structural relaxation $\beta$-processes was determined on the basis of the results obtained in both methods.

*Acknowledgements:* The financial support of the Silesian University (grant BS/ICH/TCH/03/04/05) is acknowledged.

[1] P. Penczek, Z. Kłosowska-Wołkowicz, *Polimery*, **1997**, *42*, 294.
[2] A. Burgath, A. Sunder, H. Frey, *Macromol Chem. Phys.*, **2000**, *201*, 782.
[3] K. Ishizu, D. Takahashi, *Polimer*, **2000**, *41*, 6081.
[4] N. Charles, Moorefield and George Newkome, *Advances in Dendritic Macromol.*, **1994**, *1*, 1.
[5] S. J. Evans, P. J. Haines, G. A. Skinner, *Thermochimica Acta*, **1996**, *77*, 278.

[6] S. H. Mansour, N. Ikladious, *Polymer Testing*, **2002**, *21*, 497.
[7] Mangeng Lu, Mija Shim, Sangwook Kim, *Eur. Polym. J.*, **2001**, *37*, 1075.
[8] E. Malmstrom, A. Hult, *Polymer*, **1997**, *38*, 4873.
[9] M. Paluch, M. Sekuła, S. Maślanka, K. Mańczyk, W. W. Sułkowski, S. Rzoska, J. Zioło, *J. Chem. Phys.*, **2004**, *120*, 2020.
[10] I. Lacik, I. Krupa, M. Stach, A. Kucma, J. Jurciova, I. Chodak, *Polym. Testing*, **2000**, *19*, 755–771.
[11] N. T. Qazvini, N. Mohammadi *Polymer*, **2005**, *46*, 9088–9096.
[12] U. Edlund, C. Albertsson, *Adv. Drug Deliver Rev*, **2003**, *55*, 585.
[13] Schrader B., Raman – IR. Atlas of Organoc Compounds; VCH – Ver – Ges, Weinheim, 1989.
[14] Hedvig P., Dielectric Spectroscopy of Polymers, Akademiai Kiado, Budapest, 1977.
[15] A. Danch, K. Lohner, M. Ungerank, F. Stelzer, *J. Therm. Anal. Cal.*, **1998**, *54*, 161.
[16] A. Danch, *J. Therm. Anal. Cal.*, **1999**, *56*, 1097–1105.