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Synthesis and Relaxation Properties of Model Oligoester – Tetrakis(5-hydroxypentyl)piromelite

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The study of polymer properties requires the synthesis and analysis of simple model compounds. The aim of this work was the synthesis and investigation one of model compounds are needed to perform the physicochemical characteristics of linear, branched and dendrite polyesters. The description of relaxations processes of model oligoesters can make it easier to interpret the dependence between the useful properties of polyesters and the molecular structure of their macromolecules. Instrumental methods as NMR, FTIR and dielectric spectroscopy, calorimetry (DSC), thermogravimetric analysis and mechanical spectroscopy are used to this goal. The structure of the synthesized tetrakis(5-hydroxypentyl)piromelite (oligoester) 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 different dielectric and DMTA α-relaxation processes for the oligoester are indispensable to determine the relaxation properties of the suitable polyesters. For the synthesized oligoester glass temperature (T_g), relaxation time (τ) and activation energy (E_a) were determined from the results of DSC, DMTA and dielectric spectroscopy.

Keywords Dielectric spectroscopy; DMTA; NMR; oligoesters

Introduction

Relaxation properties of unsaturated linear, hyperbranched and dendrite polyesters depend on a microstructure of polymer. Although these compounds differ with the structure each kind of polyester contains characteristic fragment with ester group. Growing of the technological and analytical possibilities cause that all the time the new solutions of the unsaturated polyesters applications are looking for. Hyperbranched and dendrites unsaturated polyesters are using to obtained alkyd resins for painting materials with lower solvents contents [1–3]. However it was noticed

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that cross-linked polymers materials after some weeks showed undesirable properties e.g., the subsurface foul and the decrease of the products surface hardness. This changes probably due to the cross-linked polymers structure. The study of the polymer microstructure often requires syntheses of low-molecular model compounds. The model compounds for polyesters are suitable oligoesters. Therefore the series of esters and oligoesters was synthesized as model compounds [4–8]. Studies of a simple model system with the use of NMR and FTIR spectroscopy, calorimetric (DSC), thermo-mechanical (DMTA) and dielectric spectroscopy methods allow us to determine the physicochemical properties of more complicated polymer systems [9,10]. Such research has made continuous improvement of the polyester production technology and the extension of their possible application [11]. However oligoester tetrakis(5-hydroxypenthyl)piromelite obtained from piromelite anhydrous and 1,5-dihydroxypentyle does not occur in the structure of unsaturated linear and dendrite polyesters, it seems important to synthesize that model oligoester and to determine its relaxation properties [12–14]. The course of the relaxation processes of the polymeric materials depends on the structure of the macromolecules. However pressure and temperature also influence this processes. The determination of the relaxation times of polymers using dielectric methods is possible only for the molecules containing polar functional groups. Polyesters are that kind of molecules [15,16].

Dynamic mechanical thermal analysis is one of the most frequently used methods for characterization of thermal, viscoelastic and structural properties of polymeric materials. The possibility to assess temperature- and time-dependent behavior, extent of phase mixing in blends, degree of crosslinking, crystalline, interfacial adhesion, ageing and degradation make this technique extremely valuable in the process of testing and designing new materials [17].

Physicochemical characteristics of the obtained ester allowed us to study the relaxation processes of polyester resin fragments. These studies may be a basis for determining the properties of polyester plastic relaxation and probably enable us to find in the future the reasons of property differences of useful linear, hyperbranched and dendrite polyester plastics [18].

The description of relaxation processes of model oligoesters can make it easier to interpret the dependence between the useful properties of polyesters and the molecular structure of their macromolecules [19].

Materials and Methodology

0,24 mol of piromelite anhydrous and 1,2 mol of 1,5-dihydroxypentyl were used to the synthesize of oligoester (Fig. 1).

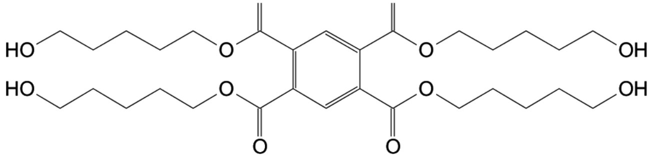

Figure 1. Tetrakis(5-hydroxypentyl)piromelite.

The mixture was heated with xylene. The product was purified by repeated washing with organic solvents and drying under vacuum over calcium chloride.

The elemental analysis was performed to determine the content of carbon, hydrogen and oxygen in about 2 mg sample of obtained oligoester by using the Automatic Elementary Analyzer CHNS-O (Perkin Elmer).

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 chloroform-d$_1$. Tetramethylenesiloxane (TMS) was an internal standard for chemical shift determination.

The analysis of DSC was performed on difference scanning calorymeter DSC Pyris 1 (PERKIN ELMER). The measurements were carried out in the range of temperature from 125 K to 374 K with heat rate 5 K/min in about 2 mg sample.

The Dynamic Mechanical Thermal Analysis spectra were recorded on analyzer Q800 DMA (TA Instruments). The technique of the study of the liquid samples of a high viscosity and amorphous samples of flow temperature (310−330 K) was not yet described. It belongs to the innovative techniques of mechanical studies. The study with the use of glass silk type was proposed by the producer of the apparatus [20]. The samples were spread on a glass silk type at ambient temperature 298 K and than cooled down. A 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 using the dynamic technique to measure parameters with constant change of temperature in the range from 123 K to 333 K with heat rate 2 K/min. At first the technique with wide range of frequencies from 1 to 120 Hz was used for precise investigation of the relaxation region.

The temperature-dependent dielectric spectroscopy measurements were carried out with Novo-Control GmbH equipment. We measured the complex permittivity over 5 decades of frequency using a Alfa analyzer (10–10^5 Hz). The temperature was controlled by the Quatro system, employing a nitrogen-gas cryostat; temperature stability at the sample was better than 0.1 K.

Results and Discussion

The elemental analysis and the FTIR spectroscopy was used to confirm the purity of the synthesized oligoester.

The results of the elemental analysis are in good agreement with the ones calculated from the assumed compositions (theoretical: C 72.68%; H 11.18%; O 16.14%; experimental: C 72.48%; H 11.02%; O 16.50%). This confirmed that the desired structure of the products was obtained.

The analysis of IR spectra showed the presence of absorption bands for the functional groups: CH_2 and CH_3 aliphatic groups; C=O ester carbonyl groups; aromatic groups. For the analysis of the obtained spectra the literature data of absorption bands for functional groups and Perkin Elmer database were used.

On the FTIR spectrum of oligoester the intensive absorption band at 1727 cm^{-1}, originating from the stretching vibration of the ester group C=O can be observed. The intensive absorption bands at 3350 cm^{-1} of –OH and at 2866 cm^{-1} of $-CH_2$ originating from the aliphatic chains of glycol can be seen (Fig. 2).

On the ^{1}H NMR spectra of oligoester the resonances of fallowing chemical shifts (δ) were observed: δ: Ar–H :$\delta = 8{,}10$ [ppm]; –(O)–CH_2–: $\delta = 4{,}17$–$4{,}01$

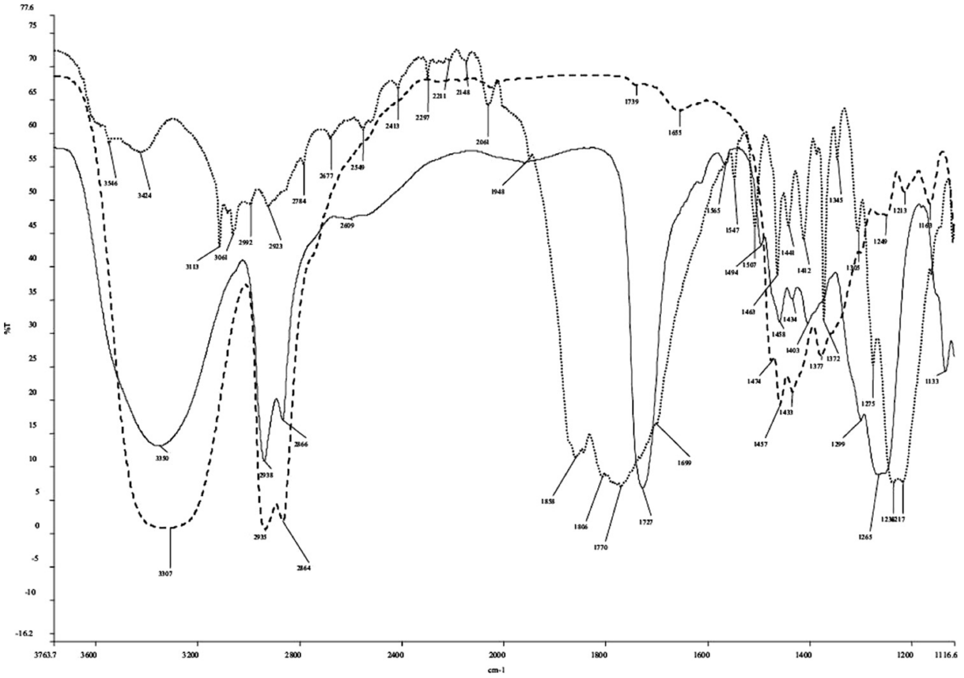

Figure 2. FTIR spectrum of oligoester ——, piromelite anhydrous ---- and 1,5-dihydroxy-penthyl ....

[ppm]; –CH$_2$–(OH) : $\delta = 3{,}70$–$3{,}53$ [ppm]; –OH : $\delta = 2{,}58$ [ppm]; –CH$_2$– : 1,30; 0,89–0,87 [ppm]; from solvent CDCl$_3$: $\delta = 7{,}27$ [ppm]; from standard TMS : $\delta = 0{,}00$ [ppm] (Fig. 3).

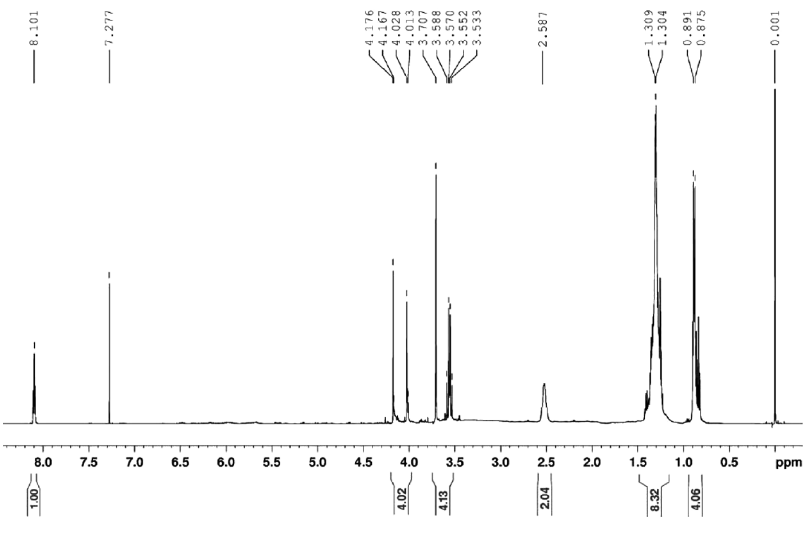

Figure 3. ^{1}H NMR (400 MHz) spectrum of oligoester.

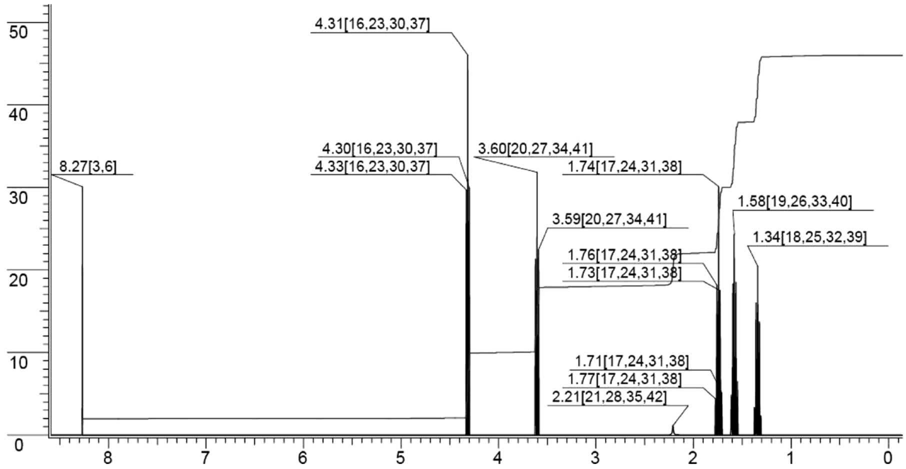

Figure 4. ^{1}H NMR computer simulation spectrum of oligoester.

The ^{1}H NMR spectroscopy were used to confirm the purity of synthesized oligoester. For the analysis of ^{1}H NMR spectra, the literature data of chemical shifts and computer simulation (ACD/HNMR Predictor 7.0) were used (Fig. 4).

On the basis of the results of the NMR analysis the relative amount of protons for each group were assigned and compared with theoretical values based on assumed structure. The theoretical number of aliphatic protons and hydroxyl groups calculated form assumed structural formula are in good agreement with the values calculated on the base of integration curves obtained from ^{1}H NMR spectra. That confirmed the assumed structure (Table 1) [21–23].

Oligoester synthesized in room temperature is liquid substance of high viscosity. It does not exhibit the tendency towards the crystallization. At the cooling down it attains the glassy state. The temperature of this transition is glass transition temperature (T_g). The determination of T_g temperature is significant for an evaluation of the temperature range for carrying out the relaxation study using DMTA and dielectric spectroscopy.

For the studied oligoester only heat effects connected with the transition from plastic to glassy state were observed i.e., glass transition temperature (T_g). T_g value determined from the DSC thermogram analysis was 198,1 K for the studied oligoester.

The results of DMTA study of oligoester (Fig. 5) showed the presence of only one α-relaxation process. This process is probably connected with the rotation of the oligoster. The explanation of this phenomenon requires further detailed studies.

Table 1. Practical and theoretical portions of oligoester protons

Group	Ar–H	–(O)–CH$_2$–	–CH$_2$–(OH)	–OH	–CH$_2$–
Quantitative theoretical portions of protons	1	4	4	2	12
Quantitative practical portions of protons	1	4,02	4,13	2,04	12,38

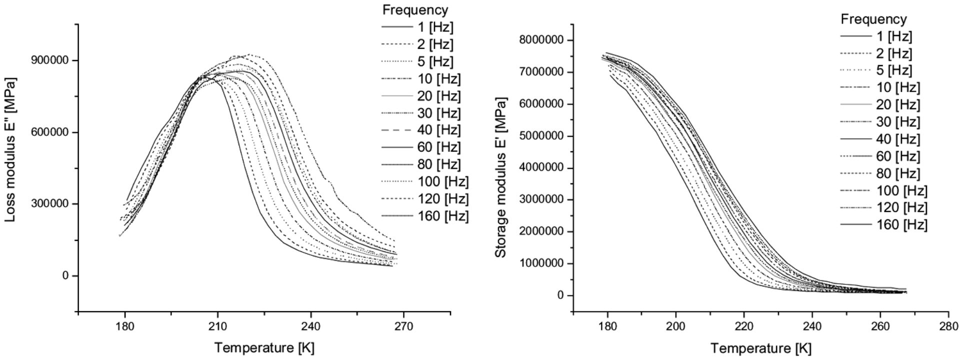

Figure 5. Temperature dependence of storage modulus E′ and loss modulus E″ oligoester for different frequency.

The results showed that the α-processes observed in DMTA study are Arrhenius processes. Their activation enthalpy H_A was defined (Fig. 6) [16].

The glass transition temperature (T_g) value was determined from the DMTA spectrum for the measurement at the frequency 1 Hz for the storage modulus E' [24]. For each studied oligoester T_g value equals 188,1 K.

In the dielectric spectroscopy studies α-relaxation process was not observed (Fig. 7). β-relaxation process is probably related to the molecular movements of aliphatic fragments of ester residues.

T_g value from dielectric spectroscopy was determined using the dependence of imaginary component of dielectric constant (ε'') on temperature for the measurement at a frequency of 1 Hz reading the temperature at peak maximum ε'' [25]. The determined T_g was 187,6 K.

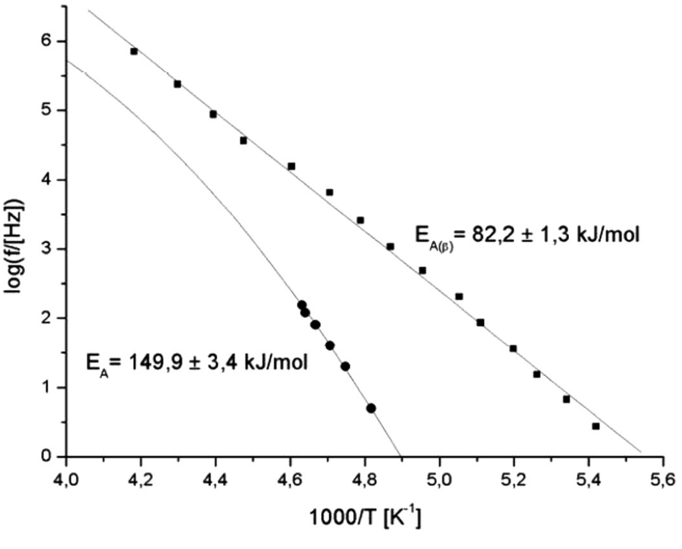

Figure 6. Arrhenius plots for the structural relaxations of oligoester for β-processes (■) results of dielectric study and α-processes (●) results of DMTA study.

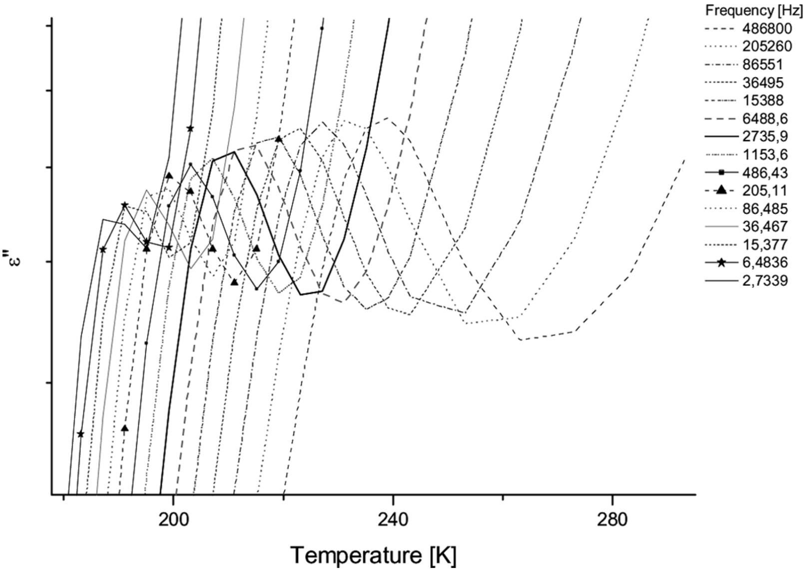

Figure 7. Loss dielectric derivative as a function of temperature for chosen frequencies for oligoester from dielectric measurements – (β-processes).

However, different temperature of the glass transition was observed in DMTA and DSC or the dielectric spectroscope methods. It is understandable because different experimental conditions were applied in all cases. The different species of energy were applied in these methods to activate relaxation processes, i.e., different speed of heating and the mass of samples [26,27].

Conclusions

The synthesis of oligoester (tetrakis(5-hydroxypentyl)piromelite) as model compound of a low molecular weight was performed.

The elemental analysis, infrared spectra and NMR spectra confirmed the desired structure and purity of the synthesized and purified oligoester.

DSC, DMTA and dielectric spectroscopy methods were used for the determination of T_g for the synthesized oligoester.

An application of New method for DMTA study allows us to determine activation energy of α-relaxation process. From the dielectric spectroscopy data activation energy of β-relaxation process was determined.

The results of the experiments allow for improving the technology of the receipt of polyesters and for the extension of the range of their application.

Acknowledgments

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