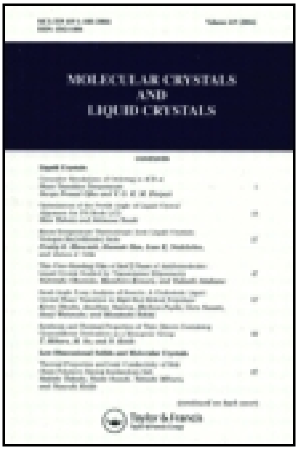

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Study of the Cross-Linking Process of Model Oligoesters by DMTA Method

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Some oligoesters were synthesized in order to study changes of the useful properties of hyper-branched unsaturated polyesters. The determination of the polymer relaxation properties allows for characterization of their structure. Useful properties of the polymers such as stability and persistence depend on their structure. The aim of the investigation was to obtain model oligoesters with low molecular weight and to study their properties by spectroscopic and the dynamic mechanical thermal analysis (DMTA) methods. The synthesis was performed with the use of ethylene glycol and the mixture of maleic anhydride and phthalic acid which allowed us to obtain linear unsaturated polyesters. The cross-linking process of synthesized model oligoesters was performed using styrene as a cross-linking agent.

The NMR and IR spectroscopy and elemental analysis were used for the description of purity and the structure of the obtained products. Relaxation properties of the synthesized oligoesters, course of their cross-linking and relaxation properties of the cross-linked products were studied by DMTA methods. In the synthesized oligoesters and cross-linked products α and β-relaxation processes were observed.

Keywords: DMTA; mechanical properties; oligoester; polyesters

INTRODUCTION

Over the last five decades continual interest in polyesters has been observed [1]. It is known that useful properties of products depend

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Address correspondence to Wiesław Sułkowski, Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, Katowice 40-006, Poland. E-mail: wieslaw.sulkowski@us.edu.pl on the microstructure of the used polymers. Research of polymer microstructure requires synthesis of low-molecular model compounds. For polyesters these models are suitable oligoesters.

Studies of a simple model system by means of NMR spectroscopy, calorimetric and thermo mechanical methods allow for the determination of the physicochemical properties of more complicated polymer systems [2,3]. Such research has led to a continuous improvement of polyester production technology and the extension of their range of usage [4,5].

In order to determine the structure of polymers and their properties, the study with the use of model low-molecular compounds was carried out. We synthesized α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid, as a fragment of a linear polyester, according to the generally accepted rules [6–8], and as a model compound for the characterization of the relaxation properties of unsaturated polyester resins [9].

Physicochemical characteristic of obtained ester facilitates a systematical study of relaxation processes of unsaturated polyester resin fragments. This study will serve as a base for qualifying polyester relaxation properties and may in the future allow us to determine the differences between useful properties observed for linear, hyperbranched, and dendritic polyester plastics. Investigation of oligoester and linear polyester plastics relaxation processes should also be the base for studying the cross-linking processes of hyperbranched and dendritic polyester. Physicochemical properties of cross-linked polyester plastics depend both on chemical structures of unsaturated prepolymers and on cross-linked copolymer particle structure. A systematic research of oligoesters ought to lead to the determination of their mutual relationships [10].

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 cross-linking, crystallinity, interfacial adhesion, ageing and degradation make this technique extremely valuable in the process of testing and designing of new materials. Nowadays the macroscopic properties of polymers and other complex materials are mainly interpreted on the basis of the underlying microscopic phenomena. Particularly, the study of 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

Bis(2-hydroxyethyl)phthalate 20 g (0,065 mol) and, bis(2-hydroxyethyl)-maleate 17,2 g (0,065 mol) and maleic anhydride 25,2 g (0,26 mol) were used to synthesize α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid (oligoester ZW) (Fig. 1). The mixture was heated with xylene until suitable quantities of water evaporated (0.43 mol = 7,6 cm^3) and then collected in an azeotropic receiver. The obtained oligoester 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. Then it was let through a molecular sieve and dried under vacuum over anhydrous calcium chloride for a period of one week under reduced pressure.

The elemental analysis was performed to determine the content of carbon, hydrogen and oxygen in 2 mg sample of the obtained oligoesters ZW. 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.

The molecular mass of oligoesters ZW was determined by the use of the cryoscopy method in Marcel OS3000 (Marcel Poland) apparatus. Dioxane was used as a solvent.

The DMTA results were obtained from analyser Q800 DMA (TA Instruments). Samples were spread on a glass silk tape in the temperature range 313 K to 318 K, then the samples were kept at ambient temperature of 293 K to cool. Glass silk tape 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 dynamics techniques 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. At first the technique with wide range of frequencies from 0.01 to 200 Hz was used for precise investigation of the relaxation region.

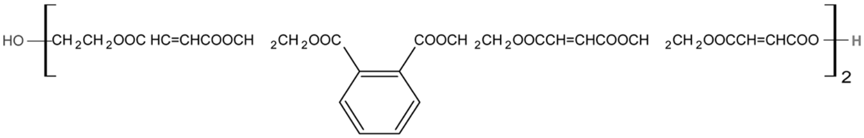

FIGURE 1 Structure of α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid – oligoester ZW.

RESULTS AND DISCUSSION

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

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.

The analysis of IR spectra showed presence of absorption bands for the following function groups: C=O carbonyl ester; C=C aromatic and C=C aliphatic. For the analysis of the obtained spectra the literature data of absorption bands for functional groups and database from spectrometer were used. The presence of the intensive absorption band at 1725 cm^{-1} characteristic for stretching vibrations of C=O group and the absence of the band at 1765 cm^{-1} characteristic for acidic C=O for oligoesters spectra were observed. For unsaturated aliphatic groups an absorption band characteristic for stretching vibrations of C=C group at 1650 cm^{-1} occurred. On the spectra of oligoester obtained from phthalic acid two absorption bands were observed at 1580 cm^{-1} and 1600 cm^{-1} characteristic for C–C vibrations from aromatic ring. Other bands present on the spectra are characteristic for deformation vibrations of groups $-CH_2-$ and $-CH_3$ and stretching vibrations of group –CH. These spectra confirm the assumed structure of the compounds [12].

The molecular mass of oligoester α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic, determined by the use of the cryoscopy method, is 1230 ± 15 g/mol. This correspondes to the theortical value of 1226.

The results of DMTA study of non-cross-linked oligoester α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid showed the presence of only one β-relaxation process (Fig. 2). This process is probably connected with the rotation of aliphatic glycol chains in the oligoester. For the α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid cross-linked by styrene the results of DMTA study showed the presence of two β-relaxation processes (Fig. 3) with the maximums of temperature at 330 K (probably connected with the rotation of cross-linked agent – styrene fragments) and 365 K (probably connected with the rotation of fragments of the polyester chain between the cross-linked nodes in the polymer chain).

For the β-relaxation processes observed with the use of DMTA methods the dependences of log ($f_{\max}$) as a function of reverse temperature (Figs. 4 and 5) was determined. The results showed that the β-processes observed in DMTA study (Figs. 2 and 3) are the Arrhenius processes. Their activation enthalpy H_A was determined.

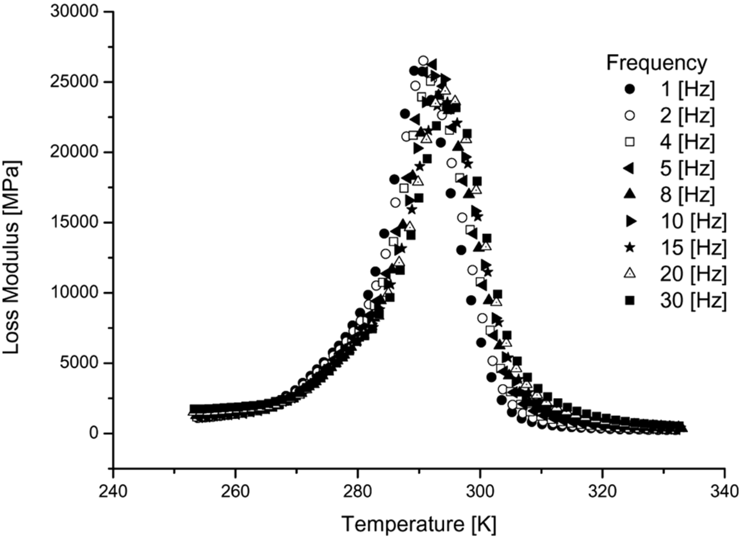

FIGURE 2 Loss modulus derivative as a function of temperature for chosen frequencies of oligoester ZW from DMTA measurements.

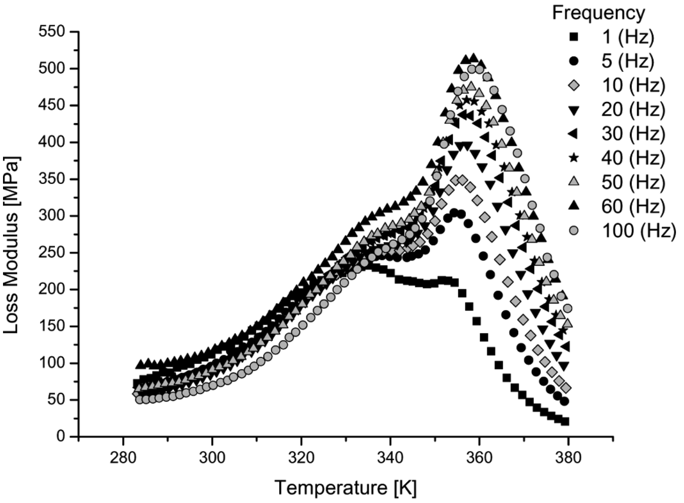

FIGURE 3 Loss modulus derivative as a function of temperature for chosen frequencies of cross-linked oligoester ZW from DMTA measurements.

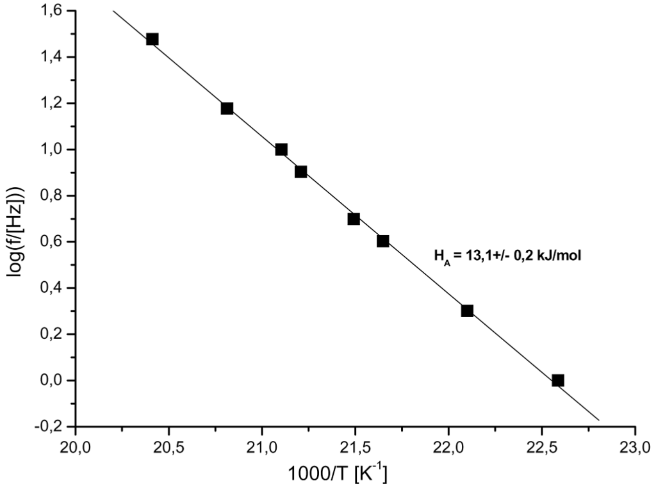

FIGURE 4 Arrhenius plots for the structural relaxations of oligoester ZW for β(■)-processes (results of DMTA Study) and calculated activation enthalpy H_A of β-processes.

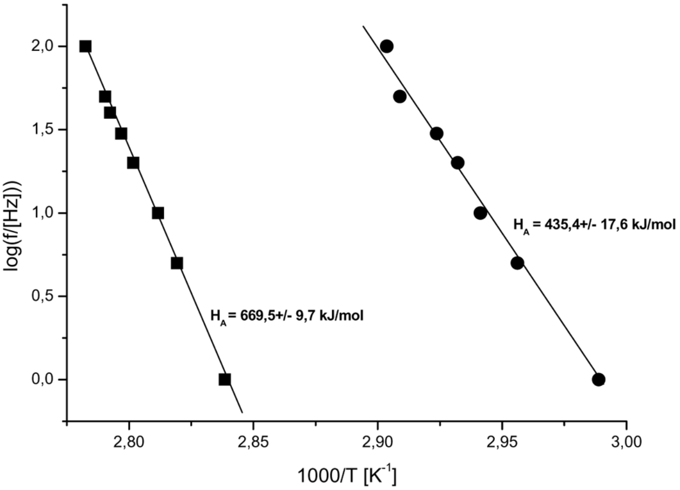

FIGURE 5 Arrhenius plots for the structural relaxations of cross-linked oligoester ZW for β (■) and β' (●)-processes (results of DMTA study) and calculated activation enthalpy H_A of β and β'-processes.

The slopes of these linear fits obey the relation [13]:

$$\log f_{\max} = \frac{A - H_A}{(2.303RT_{\max})}$$

where R – gas constant and H_A – activation enthalpy of the simple phase.

The activation enthalpy data of β-relaxation process of non-cross-linked oligoester was 13,1 ± 0,2 kJ/mol. For cross-linked oligoester the activation enthalpy of β-relaxation process data was 435,4 ± 17,6 kJ/mol for styrene fragments rotation and 669,5 ± 9,7 kJ/mol for fragments of polyester chain between the rotation of cross-linked nodes.

CONCLUSIONS

The results of elemental analysis, infrared spectra and molecular mass value determined by cryoscopy method confirmed that the synthesized and purified α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid has the desired structure and purity.

The relaxation studies with dynamic mechanical thermal analysis were performed for α-hydroxy-di(ethylmaleatethylphthalate-ethylmaleatethylmaleate)-ω-carboxylic acid. They allowed us to determine the activation enthalpy of structural relaxation β-processes.

The description of the relaxation process of a model oligoester can make it easier to interpret the dependence between useful properties of polyesters and the molecular structure of their cross-linked macromolecules [14].

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