J Therm Anal Calorim (2010) 102:1051–1055
DOI 10.1007/s10973-010-0838-1

Study of dynamics of the cross-linking process of hyperbranched polymers

S. Maślanka · W. W. Sułkowski · A. Sułkowska

Received: 10 January 2010 / Accepted: 22 April 2010 / Published online: 7 May 2010

Abstract The description of polymer relaxation properties makes it possible to characterize the influence of polymer structure on its useful properties, i.e., stability and resistance. To determine the profile of the relaxation properties of the linear, hyperbranched and dendrite unsaturated polyester resins, the synthesis of the oligoester as the model compounds was performed. The structures of the obtained model compound were confirmed by elemental analysis and ^{1}H NMR and FTIR spectroscopy. The determination of the α relaxation processes for model oligoester allowed us to describe the practical properties of commercial compounds. The description of the relaxation process may facilitate the interpretation of the dependence between useful properties of polyesters and their molecular structure. The results of the experiments allowed us to improve the technology of the synthesis processes and to extend the range of their usage.

Keywords Hyperbranched polyesters · NMR · FTIR · DMTA · Structural relaxation properties

Introduction

One of the ways to characterize the influence of the polymer structure on its useful properties, i.e., stability and resistance is the determination of the relaxation properties of the polymers. Synthesis and investigation of model compounds are required to perform the physico-chemical characteristics of polymers. Instrumental techniques such as NMR, dielectric spectroscopy, thermogravimetric analysis and mechanical spectroscopy are used to study the physico-chemical characteristic of the polymers synthesized as the model compounds [1, 2].

Dynamic mechanical thermal analysis (DMTA) is one of the most frequently used methods for determination of 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, aging and degradation makes this technique extremely valuable for the process of testing and designing 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 the molecular mobility and final properties of polymers [3–5].

The results of the experiments allow for the improvement of the technology of designing new processes and the extension of the range of their use. The obtained polymers are more stable and more resistant to degradation [6].

Esters and oligoesters prepared from glycoles, carboxylic acids, and unsaturated fatty acids are the suitable model compounds for polyesters characterization. Therefore, the synthesis of chosen esters and oligoesters as the model compounds was performed and the results were published [7–11].

In our study the oligoesters as model compounds for the hyperbranched and dendric unsaturated polyester resins were synthesized. For the synthesis 2,2-dimethylolpropionic acid, tris(methylol)propane and linoleic acid were

---

S. Maślanka · W. W. Sułkowski (✉)
Department of Environmental Chemistry and Technology,
Institute of Chemistry, University of Silesia, Szkolna 9,
40-006 Katowice, Poland
e-mail: wieslaw.sulkowski@us.edu.pl

A. Sułkowska
Department of Physical Pharmacy, Medical University
of Silesia, Jagiellońska 4, 41-200 Sosnowiec, Poland

used as substrates [12–14]. The structures of the obtained model compounds were confirmed by the elementary analysis and ^{1}H NMR and FTIR spectroscopy. Molecular masses of oligoesters were determined by the cryometeric method in 1,1,2,2 tetrabromoethane.

Relaxation properties of the selected model oligoester as well as the cross-linking processes of hyperbranched model oligoester were studied by DMTA method. Activation energy for all identified relaxation processes was determined [15].

The description of relaxation processes of model oligoester can make it easier to interpret the dependence between the useful properties of polyesters and the molecular structure of their macromolecules [16].

Experimental

Materials and methodology

0.15 mol of 2,2-dimethylolpropionic acid (bis-MPA) and 0,05 mol of tris(methylol)propane (TMP) were used to the synthesize of oligoester HTPL32 (Fig. 1). The mixture was heated with xylene. The obtained intermediate product was esterificated with 0.15 mol of linoleic acid. 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 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$_1$. Hexamethyldisiloxane (HMDSO) was an internal standard for chemical shift determination.

The molecular mass of oligoester HPTL32 was determined by the use of the cryoscopy method in Marcel OS3000 (Marcel Poland apparatus). 1,1,2,2 tetrabromoethane was used as the solvent.

The DMTA spectra were recorded on analyzer Q800 DMA (TA Instruments). The samples were spread on a glass silk type at ambient temperature 293 K to cool. 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 to 333 K with heat rate 2 K/min. The later technique was used for precise investigation of the relaxation region with a wide range of frequencies from 1 to 120 Hz. The studied samples were not taken out of measuring head of the device until all the measurements were completed. During that time the oxygenic process of cross-linking took place. Zirconium siccative in the quantity of 0.1 wt% was applied as accelerant. Glass silk type with the investigated oligoester HPTL32 was kept in the Petri dish for 240 days on air being exposed to oxygen. After 1, 4, 30, 40, 100 and 240 days the DMTA spectra were recorded. The number of the samples (1, 4, 30, 40, 100 and 240) corresponds with the number of the days of exposure.

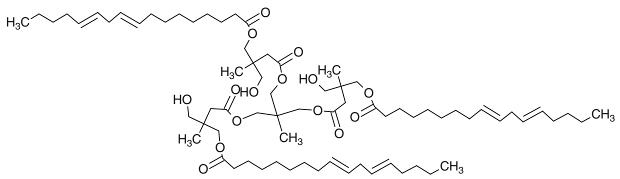

Fig. 1 Structure of oligoester HPTL32 ($C_{74}H_{126}O_{15}$)

Results and discussion

The elemental analysis and the FTIR spectroscopy were used to confirm the purity of the synthesized oligoester HPTL32.

The results of the elemental analysis are in good agreement with the ones calculated from the assumed compositions (theoretical: C 70.78%; H 10.11%; O 19.11%; experimental: C 70.60%; H 10.00%; O 19.40%). 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: C=O ester carbonyl groups; C=C aliphatic groups; CH and CH$_3$ aliphatic 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 HPTL32 the intensive absorption band at 1740 cm^{-1}, originating from the stretching vibration of the ester group C=O can be observed. The intensive absorption bands at 2930, 1655 and 1370 cm^{-1} of vibration of C=C groups, at 2855 cm^{-1} of –CH and at 1130 cm^{-1} of –CH$_3$ originating from the aliphatic chains of fatty acids can be seen (Fig. 2).

The molecular mass of oligoester HPTL32 determined with the use of the cryoscopy method is 1260 ± 10 g/mol. This corresponds to the theoretical value which is 1255.8.

On the ^{1}H NMR spectra of oligoester HPTL32 the resonances of following chemical shifts (δ) were observed: –HC=CH–: $\delta = 5.35$ (ppm); –(O)–CH$_2$–: $\delta = 4.21$–4.18 (ppm); –OH: $\delta = 4.00$ (ppm); –CH$_2$–(OH): $\delta = 2.31$–2.28 (ppm); –CH$_2$–: $\delta = 2.76$; 2.05–2.04; 1.29 (ppm); –CH$_3$: $\delta = 0.88$–0.87 (ppm) (Fig. 3).

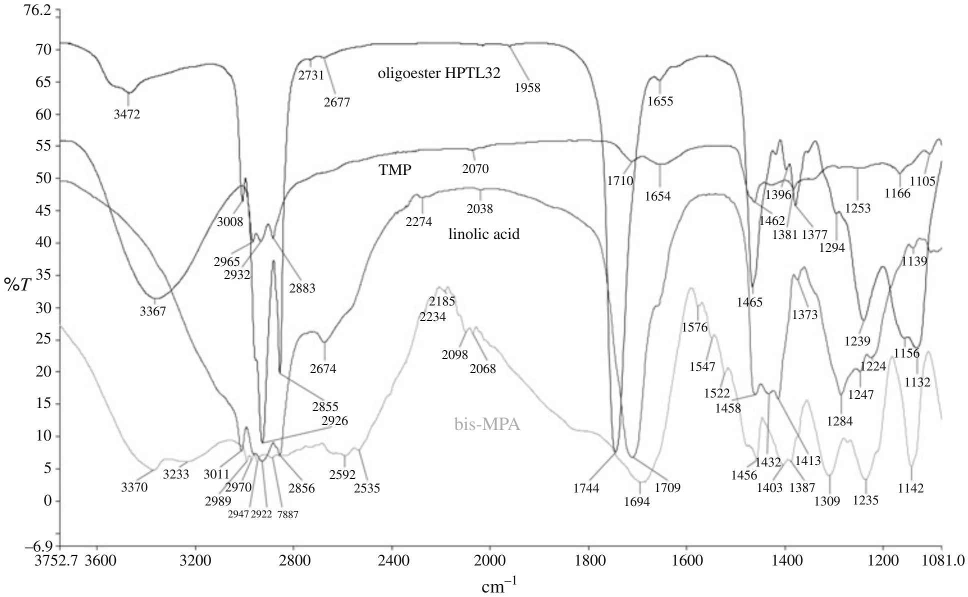

Fig. 2 FTIR spectra of oligoester HPTL32, TMP—tris(methylol)propane, linoleic acid, bis-MPA—2,2-dimethylolpropionic acid

The ^{1}H NMR spectroscopy was used to confirm the purity of synthesized oligoester HTPL32. For the analysis of ^{1}H NMR spectra, the literature data on 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 based on integration curves from ^{1}H NMR spectra, what confirmed the assumed structure (Table 1) [17–20].

The results of DMTA study of non-cross-linked oligoester HPTL32 (Figs. 5 and 6, sample 0) showed the presence of only one β-relaxation process with the maximum at 210 K. This process is probably connected with the rotation of aliphatic chains of linoleic acid in the oligoester. The spectra of the same samples changed with time (Figs. 5 and 6, samples: 1, 4, 30, 40). During incubation of a sample in air for 40 days the temperature of the maximum of β-relaxation shifts amounting 275 K (Fig. 6). Since the cross-linking process is the only change in the sample being incubated, the gradual shift after 1, 4, 30, and 40 days could be explained by this process. For a longer incubation, i.e., for the samples 100 and 240 the temperature of the maximum of β-relaxation processes does not already change. It probably points to the end of the cross-linking process. In the case of sample 240 two additional maxima on the spectra were observed. This could be the result of the cracking of the oxygen bridges due to the

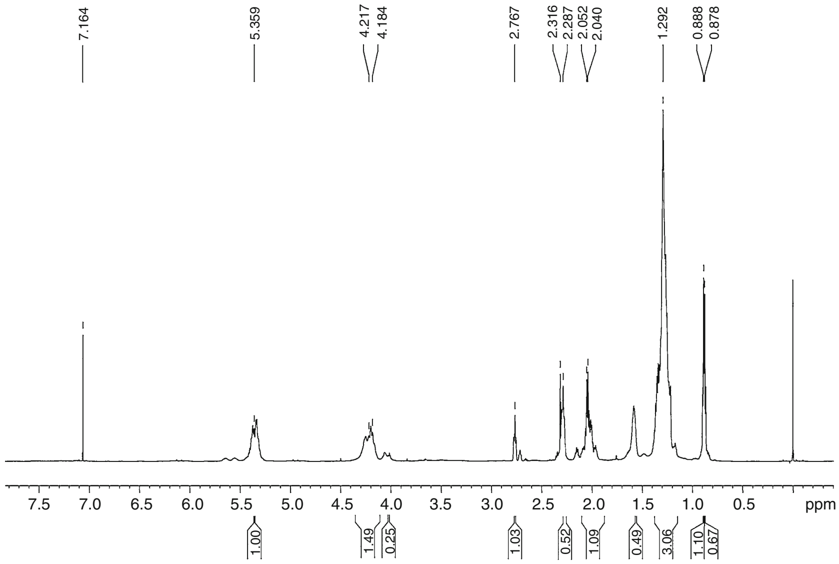

Fig. 3 ^{1}H NMR spectrum of HPTL32

Fig. 4 ^{1}H NMR computer simulation spectrum of HPTL32

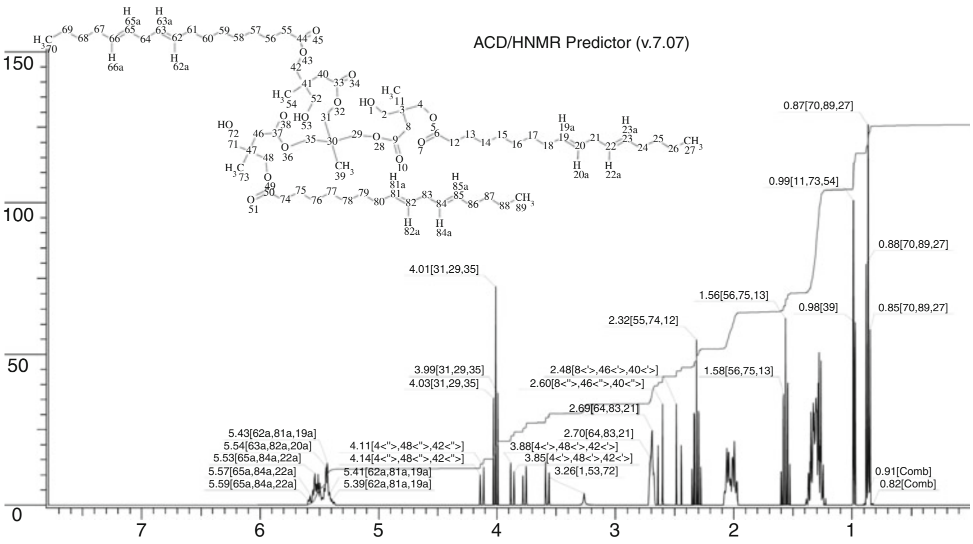

Table 1 Theoretical and experimental portions of oligoester HPTL32 protons, formula: $C_{74}H_{126}O_{15}$

Group	–HC=CH–	(O)–CH$_2$–	–OH–	–CH$_2$–(OH)	–CH$_2$–	–CH$_3$
Quantitative theoretical portions of protons	4	8	1	2	20	7
Quantitative experimental portions of protons	4	6	1	2.1	20.6	7.1

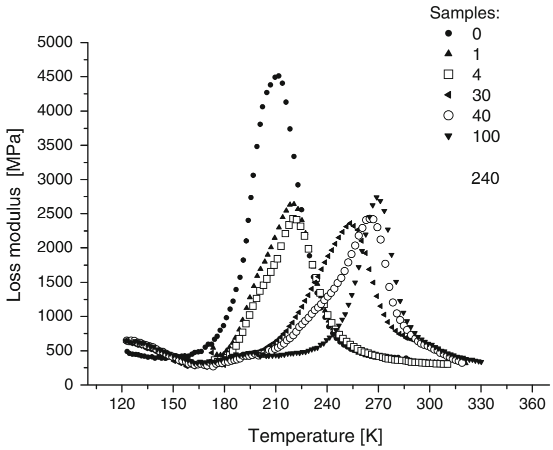

Fig. 5 Temperature dependence of loss modulus derivative for chosen frequency (1 MHz) for HPTL32 oligoester during the cross-linking process

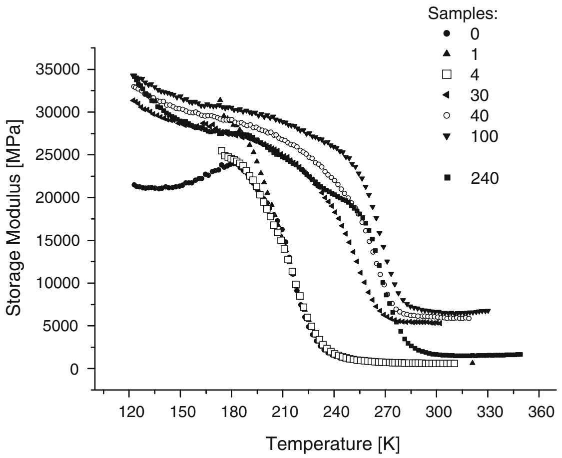

Fig. 6 Temperature dependence of storage modulus for chosen frequency (1 MHz) for HPTL32 oligoester during the cross-linking process

change of the internal structure of the cross-linked material. The explanation of this phenomenon requires further detailed studies.

For the β-relaxation processes observed with the use of DMTA methods the dependence of log ($f_{\max}$) as the function of reverse temperature (Fig. 7) was determined. The results showed that the β-processes observed in DMTA study (Fig. 5) are Arrhenius processes. Their activation enthalpy H_A was defined (Table 2).

The slopes of these linear fits obey the relation [15, 16, 21, 22]:

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

where R is the gas constant, H_A is the activation enthalpy of the simple phase.

Conclusions

The elemental analysis, infrared spectra, and ^{1}H NMR spectra confirmed the desired structure and purity of the synthesized oligoester HPTL32.

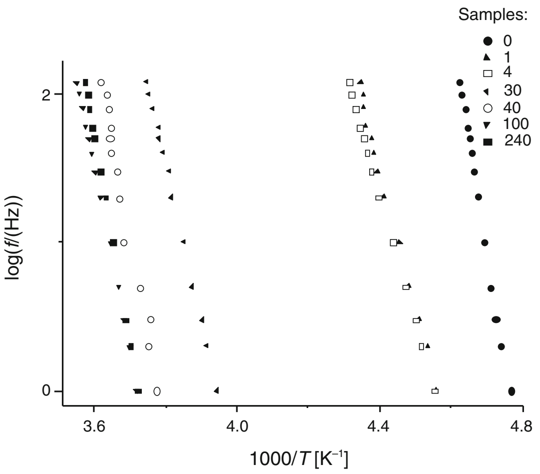

Fig. 7 Arrhenius plots for the structural relaxations of oligoester HPTL32 for β-processes (results of DMTA study)

Table 2 Calculated activation enthalpy H_A of β-processes for oligoester HPTL32

Name of sample— (days after start of measurement)	Activations enthalpy H_A (kJ/mol)
0	287.6 ± 5.4
1	177.8 ± 4.5
4	163.8 ± 1.4
30	199.6 ± 3.7
40	248.7 ± 14.3
100	266.9 ± 1.9
240	233.3 ± 2.9

The relaxation studies with DMTA were performed for oligoester HPTL32, and the activation enthalpy of structural relaxation β-processes was determined on the basis of the results obtained with these methods. The description of process relaxations of model relationships can make easy the interpretation of the dependence between useful proprieties of polyesters and with the molecular structure their macromolecules [23].

The results of the experiments allow improving the technology of the polyester synthesis. The change of the technology should affect the extension of the polyesters application. Moreover, the obtained polymers are more stable and more resistant to degradation while use.

Acknowledgements This study was supported by the Committee of Scientific Research in Poland, University of Silesia in Katowice, Poland (BS/ICh/08/09), and Medical University of Silesia (KNW-008/09).

References

1. Evans SJ, Haines PJ, Skinner GA. Thermochim Acta. 1996;77:278.
2. Mansour SH, Ikladious N. Polym Test. 2002;21:497.
3. Qazvini NT, Mohammadi N. Polymer. 2005;46:9088.
4. Jasińskal L, Balas A, Haponiuk JT, Nowaczyk G, Jurga S. J Therm Anal Calorim. 2007;88:419.
5. Bagdi K, Molnar K, Pukanszky B, Pukanszky B. J Therm Anal Calorim. 2009;98:825.
6. Sengwa R, Chuddar SC. Polymer. 2002;43:1467.
7. Maślanka S, Paluch M, Sułkowski WW, Roland CM. J Chem Phys. 2005;122:084511.
8. Maślanka S, Sułkowski WW. Annals of the polish chemical society, 2005;416.
9. Maślanka S, Sułkowski WW. Mod Polym Mater Environ Appl. 2006;2:101.
10. Sułkowski WW, Maślanka S, Pentak D, Wolińska A, Janeczek H, Paluch M, Sułkowska A. Macromol Symp. 2007;247:405.
11. Sułkowski WW, Maślanka S, Sułkowska A, Nowak K. Mol Cryst Liquid Cryst. 2008;483:155.
12. Nalampang K, Jonson A. Polymer. 2003;44:6103.
13. Diakoumakos C, Jones F. Polymer. 2001;42:2277.
14. Edlund U, Albertsson C. Adv Drug Deliv Rev. 2003;55:585.
15. Danch A. J Therm Anal Calorim. 1999;56:1097.
16. Danch A. J Therm Anal Calorim. 2001;65:525.
17. Fradet A, Marechal E. Polimery. 1985;30:141.
18. Grobelny J, Kotas A, Jedliński ZJ. Polimery. 1995;40:640.
19. Grobelny J. Polimery. 1999;44:326.
20. Tekely P. Polimery. 1982;27:137.
21. Hutchinson JM. J Therm Anal Calorim. 2009;98:579.
22. Zetterlund PB, Johnson AF. Thermochim Acta. 1996;289:209.
23. Malmstrom E, Hult A. Polymer. 1994;38:4873.