

EFFECT OF HYDROLYSIS ON MOLAR MASS AND THERMAL PROPERTIES OF POLY(ESTER URETHANES)

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Abstract

Effect of hydrolysis time on molar mass, glass transition temperature, crystallinity, and resistance to thermooxidation at elevated temperatures was analyzed for Estanes 54600, 54610, and 54650. Kinetics of the hydrolysis can be plausibly described in terms of the first-order reaction with an average induction period of about 7 days. Reduction of molar mass induced by hydrolysis brings about an appreciable decrease in glass transition temperature, fraction of crystalline domains of soft segments, and thermooxidative stability. The latter effect is manifested by shortening of the lifetimes (related to 5% mass loss) the temperature dependence of which obeys the Arrhenius plot. The observed differences in hydrolysis resistance of Estanes can be related to their chemical composition.

Keywords: hydrolysis, lifetimes, polyurethanes, thermal stability

Introduction

The segmented polyurethanes (PURs) are a broad class of polymers consisting of hard (rigid) urethane segments and soft (flexible) segments which are mostly of polyether or polyester type. The types and lengths of soft segments, which are joined by hard segments, determine whether the polyurethane will be rubbery or glassy at room temperature. In the course of their service life, PURs may undergo hydrolysis, solvolysis, thermal degradation, thermooxidation, photooxidation, etc. [1]. Many PURs are exposed to water, water solutions, water dispersions, etc., which cause their partial hydrolysis, particularly at elevated temperatures [2–9]. Of the various bonds present in PURs, the most susceptible to hydrolysis is the ester which reverts to the carboxylic acid and alcohol. The produced acid further catalyses the ester hydrolysis so that the

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autocatalytic reaction becomes prevalent [1, 7]. The hydrolysis of urethane group is by one order of magnitude slower so that its effect on molar mass decrease in poly(ester urethanes) is practically negligible. Kinetics of hydrolytic ageing of poly(ester urethane) elastomers in water was successfully treated as a pseudo-first-order reaction [7]. Though the percentage of hydrolyzed ester groups is small, they account for a significant reduction of average molar mass and, consequently, for modification of physical properties. To slow down the hydrolysis of polyester segments, polycarboimides are added to PURs which act as acid scavengers and suppress the autocatalytic effect [1].

Thermal degradation of PURs begins around 150°C by dissociation of urethane groups to the isocyanate and polyol (polyester or polyether) [1]; at about 210°C the urethane linkage cannot be detected any more and thermodegradation proceeds via several possible mechanisms [1, 11, 12]. In the case of thermooxidation, the weak link is the ether, as polyether segments are particularly prone to oxidation [1]. Thus, tendency can be observed to synthesize polyurethanes with hydrolytic and thermooxidative stability [12, 13]. On the other hand, thermodegradable polyurethanes having azo groups in the main chains are believed to facilitate the disposal of polymer wastes [14].

Parallel studies of hydrolytic and thermal stability of PURs have been rather rare until now [12, 13, 15] though both characteristics are of extraordinary importance in demanding applications. However, no data are available on how the proceeding hydrolysis affects thermal stability of PURs. For this reason, we have undertaken a complex study of Estanes 54600, 54610 and 54650 which can be viewed as certain 'standards' of thermoplastic PURs due to their large-scale applications. Hydrolysis stability of similar poly(ester urethanes) was tested [5] earlier in water at 70°C up to 8 weeks. However, test specimens were kept in test tubes in a relatively small amount of water; as the acid products of PUR hydrolysis accelerate the hydrolysis, the conditions were not unique for all specimens.

The objective of this communication was to analyze the effect of the hydrolysis time on molar mass, glass transition temperature, and resistance to thermal degradation of Estanes. The samples were used in two different values of thickness in order to ascertain the effect of sheet thickness on the hydrolysis rate and produced changes in thermal properties. This communication is a part of a comprehensive study [16] encompassing also the effect of hydrolysis on viscoelastic and ultimate properties of Estanes and new types of poly(ether urethanes).

Experimental

The studied poly(ester urethanes) are produced by Goodrich and commercially available under the trade names Estane 54600, 54610 and 54650. Their

^1H - and ^{13}C -NMR analysis [17] has shown that the amount of hard segments consisting of diphenylmethane-4,4'-diisocyanate (MDI) decreases with the product number, while molar mass of soft segments increases. However, polyester segments of Estanes 54600 and 54610 consist of adipic acid and 1,4-butanediol, while those of Estane 54650 are synthesized from adipic acid and 1,6-hexanediol. The chain extender is identical in all species, i.e., 1,4-butanediol.

Test specimen were cut from the sheets 0.3 and 1.5 mm thick of Estanes processed by Chiorino, Biella, Italy. As the hydrolysis stability of Estanes should be compared under identical conditions, test specimens were stored at 70°C for 1, 2, 4, and 8 weeks in a great surplus of distilled water (about 30 liters for specimens of total weight of about 290 grams, i.e., 10 grams of PUR per liter of water). After the exposure, the specimens were stored 3–4 months at room temperature; before the DSC measurements they were dried in vacuo for three days at 50°C until a constant mass was achieved.

Intrinsic viscosity $[\eta]$ was determined at 25.0°C by using an Ubbelohde viscometer (type I). The solutions of various concentrations of PUR in N,N-dimethyl formamide were prepared by diluting the initial solution containing about 160 mg of a PUR in 100 ml of solution.

Thermal properties

A differential scanning calorimeter Mettler DSC 30 was used to determine the glass transition temperature, T_g , of amorphous parts and the heat of fusion of crystalline domains formed by polyester segments. The conditions of the DSC measurements were as follows: temperature interval: -100 to 100°C; heating or cooling rate; 10 deg·min⁻¹; specimen weight: about 20 mg; nitrogen flux: 100 ml/min. Thermogravimeter Mettler TG50 was used to evaluate the effect of the hydrolysis time in water on thermal stability (thermooxidation) of PURs. The lifetimes up to 5% mass loss were determined in air (flux: 200 ml/min) at several temperatures in the interval 220–370°C.

Results and discussion

Molar mass, M_v , was calculated by using the Mark-Houwink equation in the following form:

$$M_{vh} / M_{vo} = ([\eta]_h / [\eta]_o)^{1/a} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, indices h and o denote the values after the hydrolysis time t_h and the initial values for $t_h = 0$; exponent $a = 0.64$ was taken

from literature [18]. The hydrolysis of ester linkages can be described [7] in terms of the first-order reaction. Each cleavage of the backbones leads to the generation of a new molecule; thus,

$$dn/dt = \rho[d(1/M)/dt] = kt_h \quad (2)$$

where n is the number of moles of macromolecules in a volume unit, ρ is the polymer density, and k is the first-order rate constant. Integration of Eq. (2) and its combination with Eq. (1) give

$$\ln(M_{vh}/M_{vo}) = \ln([\eta]_h/[\eta]_o)^{1/2} = -k(t_h - t_i) \quad (3)$$

where t_i is the induction period of hydrolysis. The data for all Estanes obey this dependence plausibly well (Fig. 1), indicating the induction period in the range between 5 and 9 days. As the dependences are very close to one another, it is obvious that the hydrolysis of the specimens proceeds in an analogous manner, even though the as-received samples differ in $[\eta]_o$ and M_{vo} . In average, M_{vh} drops to 15% of initial values after 8 weeks of hydrolysis. The difference in sample thickness does not seem to have any pronounced effect on the molar mass of hydrolyzed samples.

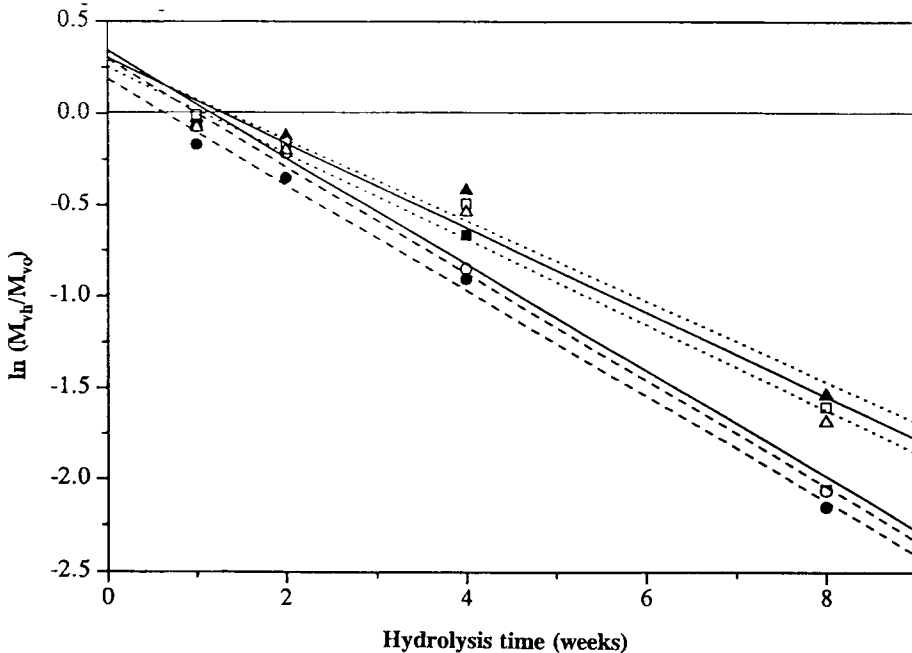


Fig. 1 Effect of hydrolysis time on relative molar mass of Estanes.

Symbols used: samples 1.5 mm: ■ (54600); ● (54610); ▲ (54650); samples 0.3 mm: □ (54600); ○ (54610); △ (54650)

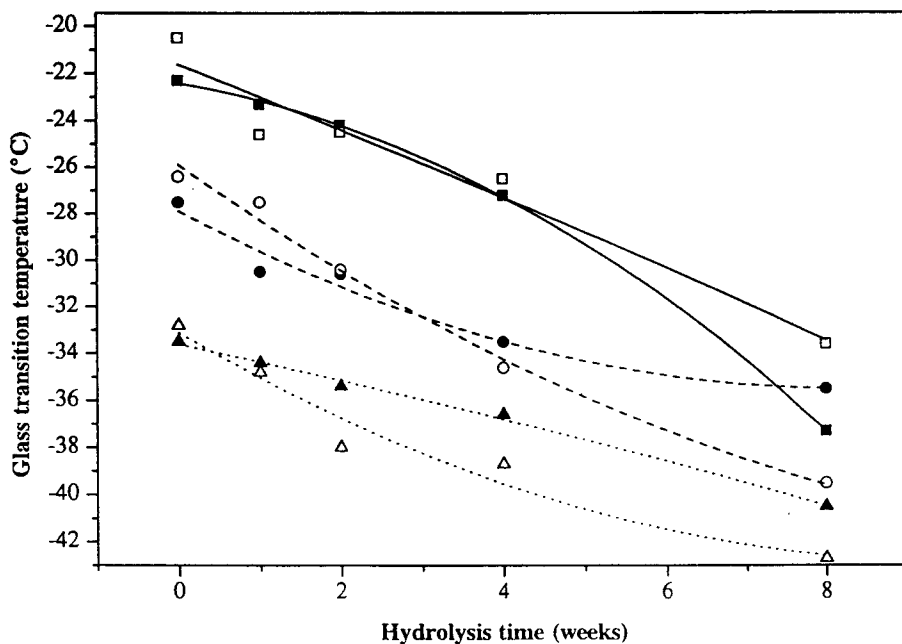


Fig. 2 Effect of hydrolysis time on glass transition temperature of Estanes. Symbols as in Fig. 1

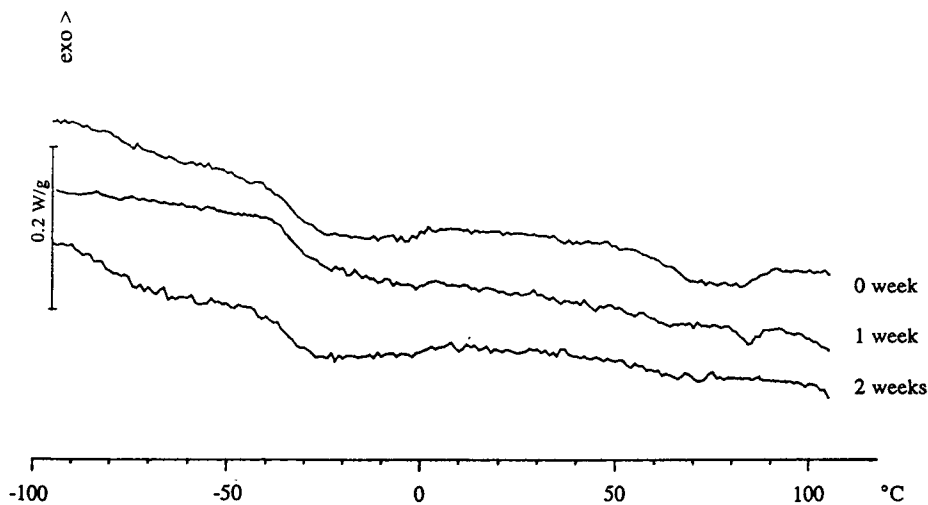


Fig. 3 Effect of hydrolysis time on DSC curves of Estane 54650

Polyester soft segments in Estanes are characterized by the glass transition temperature $T_g = -20 \div -34^\circ\text{C}$ (Fig. 2) and by the melting of crystalline do-

mains at $T_m = 70 \div 80^\circ\text{C}$ (Fig. 3). The lowest T_g of Estane 54650 is attributable to relatively lower polarity of soft segments due to the presence of 1,6-hexanediol. The cause of higher T_g of Estane 54600 – in comparison to Estane 54610 – can be sought in higher fraction of hard domains which act as physical crosslinks and represent sterical hindrances to the molecular mobility of soft segments. Figure 2 also shows that T_g decreases markedly with the time of hydrolysis. To describe the effect of molar mass of homopolymers on their T_g , the following relation was proposed [19]:

$$T_g = T_g^\infty - C / M \quad (4)$$

where T_g^∞ is the glass transition temperature at 'infinite' molar mass and C is an experimental constant. If T_{go} and T_{gh} characterize as-received and hydrolyzed specimens, respectively, the Eq. (4) can be rearranged into the following form:

$$(T_{go} - T_{gh}) / T_{go} = (C / M_{vo} T_{go})(M_{vo} / M_{vh} - 1) \quad (5)$$

Our experimental data plotted in Fig. 4 are in plausible agreement with the predicted tendency, though they do not fit straight lines, particularly at longer pe-

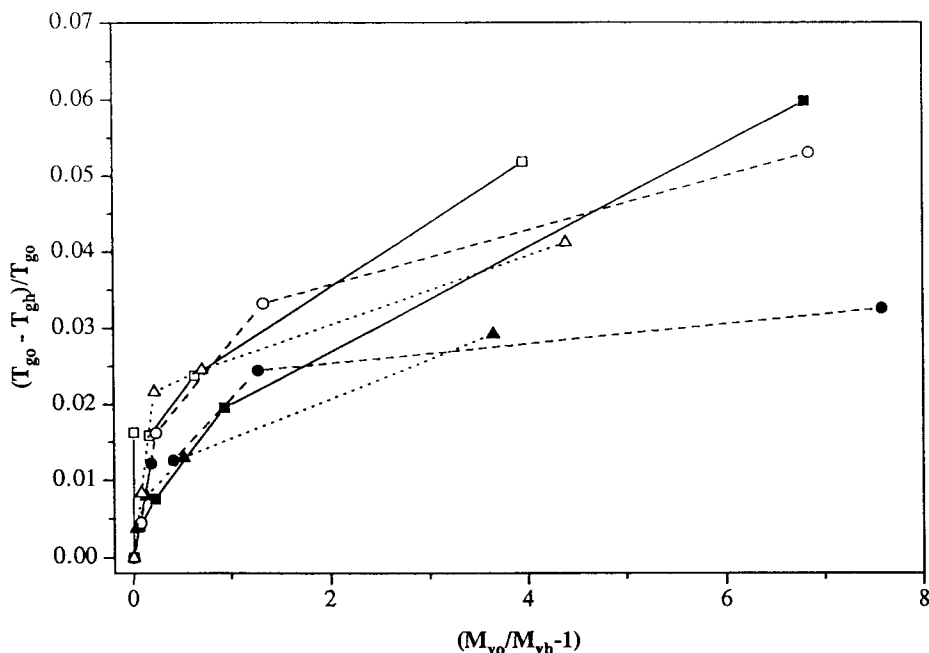


Fig. 4 Effect of relative molar mass on relative changes in glass transition temperature. Symbols as in Fig. 1

Table 1 Effect of hydrolysis time on parameters of the Arrhenius Eq. (6)

Hydrolysis time	Thickness 1.5 mm			Thickness 0.3 mm		
	0 weeks	4 weeks	8 weeks	0 weeks	4 weeks	8 weeks
A	-11.41416	-12.25902	Estane 54600 -12.78493	-13.76196	-14.94557	-15.38675
$\Delta H / \text{J}\cdot\text{mol}^{-1}$	0.87869	0.92725	0.95461	1.00621	1.07141	1.09640
A	-14.31766	-15.23889	Estane 54610 -15.44712	-15.30149	-15.27577	-16.38756
$\Delta H / \text{J}\cdot\text{mol}^{-1}$	1.06418	1.12205	1.11761	1.10028	1.08776	1.15759
A	-11.44464	-12.68298	Estane 54650 -12.99749	-13.89584	-14.59027	-14.64886
$\Delta H / \text{J}\cdot\text{mol}^{-1}$	0.88518	0.95836	0.97092	1.02127	1.05728	1.05659

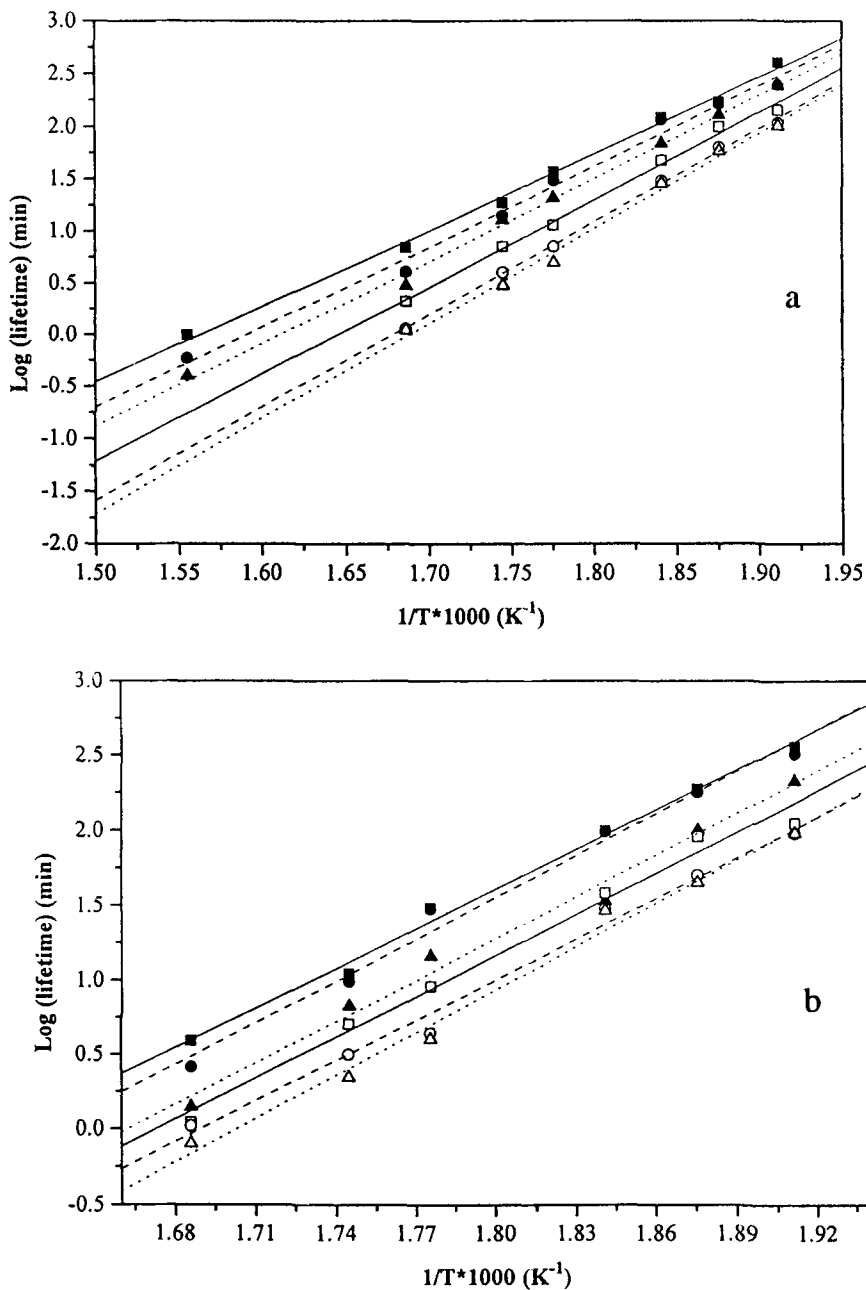


Fig. 5 Arrhenius plot of the lifetimes vs. the reciprocal absolute temperature
 (a) 54600; (b) 54650. Symbols used: samples 1.5 mm, hydrolysis time (weeks): ■,
 (○); ● (4) ▲ (8); samples 0.3 mm, hydrolysis time (weeks): □ (0); ○ (4); △ (8)

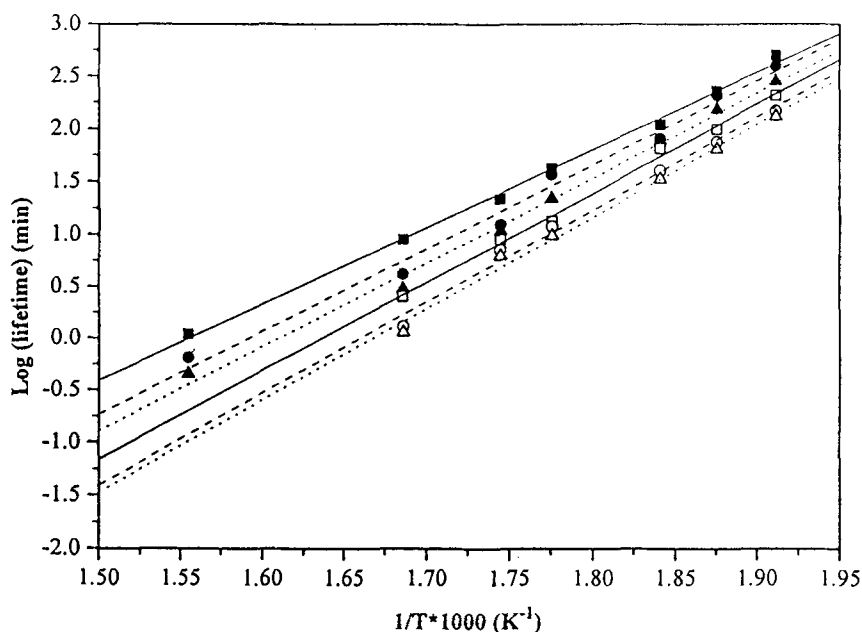


Fig. 5 Continued (c) 54650.

Symbols used: samples 1.5 mm, hydrolysis time (weeks): ■ (0); ● (4) △ (8); samples 0.3 mm, hydrolysis time (weeks): □ (0); ○ (4); △ (8)

riods of hydrolysis, presumably because PURs are not homopolymers, but segmented polymers.

Melting of crystalline domains of polyester segments is detected at about $T_m = 72^\circ\text{C}$ (Fig. 3). The area of the melting peak is markedly reduced after 1 week of hydrolysis and the peak disappears after 2 weeks of hydrolysis. It is likely that the crystalline domains are melted at the temperature of hydrolysis (70°C) so that the hydrolytic cleavage of ester groups is evenly distributed in the whole volume of the specimen. However, as the decrease in molar mass during the first week of hydrolysis is almost negligible, the crystallinity reduction is to be primarily ascribed to kinetic reasons which prevent the reconstitution of crystalline domains after the exposure to water, i.e., in the course of long-term storage at room temperature and drying at 50°C . A perceptible decrease in molar mass after 2 weeks of hydrolysis obviously prevents — along with kinetic reasons — any crystallization of soft segments. This destruction of crystalline domains has a profound effect on elastic and ultimate mechanical properties of Estanes [16].

The thermogravimetric data for all specimens of Estanes fit quite well (Figs 5a,b,c) the Arrhenius plot which is one of the equations [20] usually used

for describing the effect of temperature on the lifetime of the samples exposed to thermal degradation:

$$\log \text{ lifetime} = A + \Delta H / RT \quad (6)$$

where A is a constant encompassing entropic effects, ΔH is the activation enthalpy, R is the gas constant, and T is the absolute temperature. The hydrolysis has a detrimental effect on the lifetimes (Fig. 6) of Estanes which is manifested (Table 1) by an appreciable drop of A and by a very small (but regular) increase in activation enthalpy. Thus, the effect of the decrease in A is partially compensated by the increase in ΔH . The latter fact indicates that the changes in temperature affect more the kinetics of thermooxidation in the hydrolyzed samples than in the as-received ones. The significant drop of A caused by the hydrolysis is probably linked to entropic effect associated with the decrease in molar mass. As the effect of sample thickness on the hydrolysis kinetics is almost negligible (Fig. 1), the shorter lifetimes of thinner samples are apparently related to the kinetics of thermooxidation. Estane 54650 displays the longest lifetimes in the whole interval of hydrolysis periods (Fig. 6). Its superior resistance to hydrolysis can be ascribed to 1,6-hexanediol which increases hydrophobicity of soft segments. The reason why Estane 54610 is characterized by shorter lifetimes

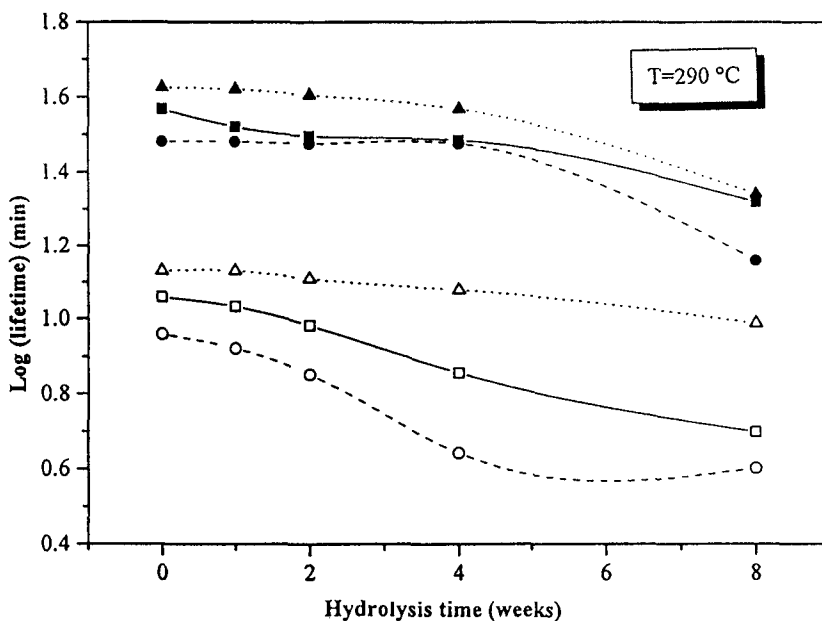


Fig. 6 Effect of hydrolysis time on thermooxidative lifetime. Temperature of TG: 290 °C. Symbols as in Fig. 1

than Estane 54600 is likely to consist in lower content of hard segments and, consequently, higher fraction of ester groups exposed to hydrolysis.

Conclusions

Thermal properties of Estanes 54600, 54610, and 54650, which rank among poly(ester urethanes), are appreciably affected by prior hydrolysis. The kinetics of the hydrolysis can be plausibly described in terms of the first-order reactions; the average induction period is about 7 days, which means that short expositions to water do not cause any perceptible changes in molar mass. Reduction of molar mass induced by the hydrolysis accounts for decrease in (i) glass transition temperature, (ii) fraction of crystalline domains constituted by soft segments, and (iii) thermal stability evaluated as the thermooxidation lifetimes (up to 5% mass loss) at elevated temperatures. Temperature dependence of the lifetimes follows the Arrhenius plot; the drop of factor A caused by the hydrolysis is partially compensated by the increase in the activation enthalpy. The observed differences in hydrolytic stability of Estanes can be related to their chemical composition.

References

- 1 V. Gajevski, 33rd An. Polyurethane Tech. Marked. Conf., 1990, p. 506.
- 2 A. Singh and L. Weissbein, *J. Polym. Sci. A-1*, 4 (1966) 2551.
- 3 G. Magnus, R. A. Dunleavy and F. E. Critchfield, *Rubber Chem. Technol.*, 39 (1966) 1328.
- 4 Z. T. Ossefort and F. B. Testroet, *Rubber Chem. Technol.*, 39 (1966) 1308.
- 5 C. S. Schollenberger and F. D. Steward, *Angew. Makromol. Chem.*, 29/30 (1973) 413.
- 6 B. Masar, P. Cefelin, T. E. Lipatova, L. A. Bakalo and G. G. Lugovskaya, *J. Polym. Sci.: Polym. Symp.*, 66 (1979) 259.
- 7 D. W. Brown, R. E. Lowry, and L. E. Smith, *Macromolecules*, 13 (1980) 248.
- 8 G. Oertel, *Polyurethane Handbook*, Hanser Publ., Munich 1985, p. 385.
- 9 T. M. Chapman, *J. Polym. Sci. A: Polym. Chem.*, 27 (1989) 1993.
- 10 N. Grassie and G. Scott, *Polymer Degradation & Stabilization*, Cambridge University Press, Cambridge 1985, p. 41.
- 11 H. H. G. Jellinek, *Degradation and Stabilization of Polymers*, Vol. 1, Elsevier, New York 1983, p. 91.
- 12 T. M. Chapman, D. M. Rakiewicz-Nemeth, J. Swestock and R. Benrashid, *J. Polym. Sci. A: Polym. Phys.*, 28 (1990) 1473.
- 13 P. A. Gunatillake, G. F. Meijs, E. Rizzardo, R. C. Chatelier, S. J. McCarthy, A. Brandwood and K. Schindhelm, *J. Appl. Polym. Sci.*, 46 (1992) 319.
- 14 Y. Shimura and D. Chen, *Macromolecules*, 26 (1992) 5004.
- 15 K. Tamareselvy, K. Venkatarao and H. Kothandaraman, *J. Polym. Sci. A: Polym. Chem.*, 28 (1990) 2679.
- 16 A. Pegoretti, J. Kolarik and A. Penati, *Angew. Makromol. Chem.*, to be published.
- 17 A. Guerriero, private communication.
- 18 V. Kasparkova and M. Bohdanecky, to be published.

- 19 J. E. Mark, A. Eisenberg, W. W. Graessley, L. Mandelkern and J. L. Koenig, Physical Properties of Polymers, Am. Chem. Soc., Washington, D. C., 1984, p. 71.
20 T. Kelen, Polymer Degradation, Van Nostrand Reinhold, New York 1983, p. 40.

Zusammenfassung — Für Estan 54600, 54610 und 54650 wurde der Einfluß der Hydrolysedauer auf die Molmasse, den Glasumwandlungspunkt, die Kristallinität und die Beständigkeit gegenüber Thermooxidation bei erhöhten Temperaturen untersucht. Die Reaktionskinetik der Hydrolyse kann einfach mit den Ausdrücken der Reaktion erster Ordnung, unter Berücksichtigung einer durchschnittlichen Induktionsperiode von 7 Tagen beschrieben werden. Die hydrolyseinduzierte Abnahme der Molmasse verursacht eine beträchtliche Verminderung des Glasumwandlungspunktes, der Fraktion der kristallinen Bereiche von Soft-Segmenten und der thermooxidativen Beständigkeit. Letzterer Effekt drückt sich in einer Verkürzung der Lebensdauer in Verbindung mit 5% Masseverlust und der Temperaturabhängigkeit aus, der die Arrhenius'sche Darstellung unterliegt. Die beobachteten Unterschiede bei der Hydrolysebeständigkeit von Estanen können mit ihrer chemischen Zusammensetzung in Verbindung gebracht werden.