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POLIMERY

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII i PRZETWÓRSTWU POLIMERÓW

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Syntheses of new poly(ester-carbonate-urethane)s based on trimethylene carbonate (TMC) and polyester polyol derived from dimerized fatty acid

Summary — A series of poly(ester-carbonate-urethane)s containing different weight ratios of respective fragments were synthesized by coupling of dihydroxyl compounds with diisocyanates. First, poly(trimethylene carbonate) diol (PTMCD) was prepared *via* ring opening polymerization of trimethylene carbonate (TMC) using 1,4-butanediol as an initiator and stannous 2-ethylhexanoate as a catalyst. PTMCD was further reacted in the melt with polyester polyol (dimer diol derived from dimerized fatty acid, DD) in the presence of hexamethylene diisocyanate (HDI) as a coupling agent. The structure and physical properties of PTMCD and final copolymer were characterized by ATR FT-IR and DSC measurements. Thermal analysis indicated that temperature transitions were dependent on the copolymer composition. The hydrolytic degradation (pH = 9.0) profiles of selected copolymers were also dependent on the polymer composition: higher weight loss was observed for polymers containing higher amount of carbonate units. At high concentration of DD (70 wt. %) the polymers showing high elasticity (330 %) were produced.

Key words: copoly(ester-carbonate-urethane)s, poly(trimethylene carbonate), chemical structure, thermal properties.

SYNTEZA NOWYCH POLI(ESTRO-WĘGLANO-URETANÓW) NA PODSTAWIE WĘGLANU TRIMETYLENU (TMC) I POLIESTROPOLIOLU OTRZYMANEGO Z DIMERYZOWANEGO KWASU TŁUSZCZOWEGO

Streszczenie — Zsyntetyzowano serię różniących się składem kopoli(estro-węglano-uretanów) metodą sprzęgania związków dihydroksylowych za pomocą diizocyjanianu heksametylenu (HDI). Na pierwszym etapie, w wyniku polimeryzacji z otwarciem pierścienia węglanu trimetylenu (TMC) przy użyciu 1,4-butanodiolu jako inicjatora i oktanianu cyny jako katalizatora otrzymano poli(węglanotrimetyleno)diol (PTMCD). PTMCD poddano następnie reakcji w fazie stopionej z poliestropoliolem (dimerodiolem pochodzącym z dimeryzowanego kwasu tłuszczowego, DD) w obecności HDI jako czynnika sprzęgającego (schemat A). Budowę chemiczną PTMCD oraz kopolimerów scharakteryzowano metodami ATR FT-IR oraz ^{1}H NMR (rys. 1 i 2). Analiza termiczna potwierdziła zależność wartości temperatury przemian fazowych kopolimerów od ich składu (tabela 2, rys. 3 i 4). Przebieg

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hydrolitycznej (pH = 9.0) degradacji wybranych kopoli(estro-węglano-uretanów) również wykazał zależność od składu: większy ubytek masy zaobserwowano w przypadku produktu zawierającego większy udział jednostek węglanowych (rys. 5). Kopolimery o znacznym udziale DD (70 % mas.) odznaczały się dużą elastycznością (330 %, tabela 3). Metodą GPC określono wartości M_n, M_w oraz M_w/M_n wybranych kopolimerów (tabela 1).

Słowa kluczowe: kopoli(estro-węglano-uretany), poli(węglan trimetylenu), budowa chemiczna, właściwości cieplne.

Biodegradable materials have been already widely used in large number of applications in packing, paper coating, fibers, as well as in medicine as implants, controlled drug delivery systems and scaffolds for tissue engineering [1—5]. Among the biodegradable polymers, much attention is paid to polyesters [6—9] especially based on polyglycolide (PGA), polylactide (PLA) and poly(ε-caprolactone) (PCL) [5—7]. Recently the materials based on cyclic carbonates, *e.g.* trimethylene carbonate (TMC), attracted attention as biodegradable polymers [13].

TMC can be polymerized chemically [8, 9] as well as enzymatically [5, 10] to produce poly(trimethylene carbonate) (PTMC) with high hydrolytic stability and degradation by surface erosion without release of acidic groups that might catalyze the hydrolysis of carbonate linkages [8].

An incorporation of aliphatic carbonate units based on TMC into segmented copolymer structure can be a successful method to modify both mechanical properties and rate of biodegradation of aliphatic polyesters. The introduction of carbonate linkages into a rigid polymer chain improves elasticity of copolymers but decreases their tensile strength [11]. Moreover, polymers based on aliphatic polycarbonate diols are promising materials with high potential for medical applications due to their biocompatibility, low toxicity and susceptibility to biodegradation [12]. Copolymerization of TMC with lactide or glycolide [8, 13—15], various lactones [16, 17], adipic anhydride [18], and cyclic imine [19] have also been reported.

Biodegradable monomers such as lactic acid or succinic acid, obtained from renewable resources, can be used in various biomedical applications due to their fast degradation. However, some applications require the use of materials with slow degradation time and PTMC can be the material of choice, but in case of molecular weight <100 kDa it shows low dimensional stability and weak mechanical properties [20]. Therefore, copolymerization of TMC with polyester polyols (dimer diols), being polymerization products of dimer fatty acids [DFA, $HOOC-(CH_2)_{34}-COOH$] with low molecular weight acids and diols known under the trade name as Priplast [21], can be an interesting and new approach in syntheses of elastomeric and mechanically stable TMC-based materials.

In this work, we present the syntheses and characterization of new aliphatic poly(ester-carbonate-urethane) copolymers composed of carbonate units from poly(trimethylene carbonate)diol (PTMCD), ester units from polyester polyol and urethane linkages formed during the coupling of dihydroxyl compounds with diisocyanate chain extender. The influence of carbonate segments content on chemical structure, physical and mechanical properties as well as hydrolytic degradation in different buffers (pH = 7.2, 5.0 or 9.0) was investigated.

EXPERIMENTAL

Materials

The following substrates were used in synthesis of poly(trimethylene carbonate)diol (PTMCD): trimethylene carbonate (TMC, Boehringer Ingelheim, Germany), 1,4-butanediol (BD, Acros Organics, the Netherlands) and tin dioctate [$Sn(Oct)_2$, Sigma-Aldrich, Germany].

In the syntheses of poly(ester-carbonate-urethane)s we used: PTMCD dimer diol (DD, commercial name Priplast 3192, molecular weight 2000 g/mol, Uniqema Croda, Holland), dibutyltin dilaurate (BDTDL, Fluka) and hexamethylene diisocyanate (HDI, Sigma-Aldrich, Germany).

Syntheses

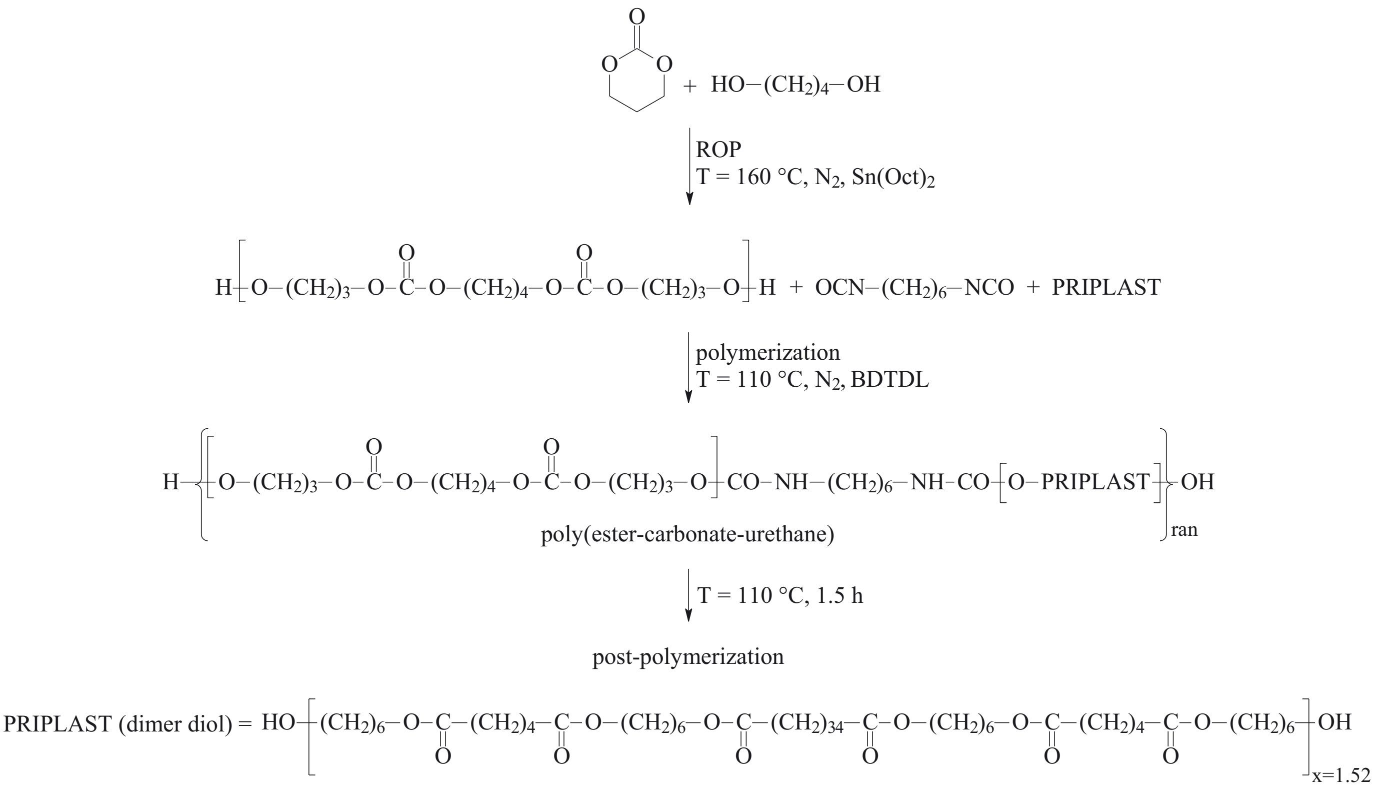
Poly(carbonate) diol (PTMCD)

The ring opening polymerization (ROP) of TMC was carried out under nitrogen atmosphere in 500 ml three necked flask. The given amounts of TMC, BD as initiator (molar ratio of monomer/initiator 39/1) and $Sn(Oct)_2$ as a catalyst (molar ratio of monomer/catalyst 100/1) were placed in a flask and heated up to 160 ^{o}C for 8 h.

The main properties of PTMCD were as follows: hydroxyl number (L_{OH}) 72.8 mg KOH/g, number-average and weight-average molecular weights 3408 Da and 6200 Da, respectively, molecular weight distribution 1.82.

Poly(ester-carbonate-urethane)s

The given amounts of PTMCD, DD and BDTDL as a catalyst (molar ratio of diol/catalyst 500/1) were heated slowly to 100 ^{o}C at constant speed of stirring. At this temperature HDI was added into a polymer melt as a coupling agent. Resulted polymers were then post-polymerized for 1.5 h at 110 ^{o}C under atmospheric pressure. Polymers with variable PTMCD/DD ratios *i.e.* 70/30,



Scheme A. Schematic representation of poly(ester-carbonate-urethane) synthesis

60/40, 50/50, 40/60 and 30/70 wt. % were synthesized. Scheme A presents the course of two-stage synthesis of poly(ester-carbonate-urethane) described above.

Methods of characterization

— All materials for further characterization were prepared as thin polymer films (0.5 mm thick) by hot process melting and then samples in a form of discs of 10 mm diameter and B5 dumbells were cut off.

— Attenuated Total Reflection Fourier Transform Infrared Spectra (ATR FT-IR) were recorded using the Nexus (Thermo Nicole Corp.) spectrometer with Single Reflection Diamond (ATR) scanning between 400—4000 cm^{-1}.

— ^1H NMR spectra were recorded using a Bruker DPX 400 MHz spectrometer. Samples for NMR measurements were dissolved in deuterated chloroform ($CDCl_3$). Tetramethylsilane (TMS) was used as an internal standard.

— Number-average and weight-average molecular weights of PTMCD (M_n, M_w, respectively) were determined by gel permeation chromatography (GPC). The GPC analyses were performed at room temperature using a Spectra Physics system from Viscotek equipped with a model 8800 pump and a model VE3580 refractive index detector (RI). THF was used as mobile phase at a flow rate of 1 ml/min and polystyrene solution in THF as a calibration standard.

— Differential Scanning Calorimetry (DSC) were performed using TA Instruments 2920 MDSC V2.6A. For DSC, the sample weight was between 10 mg and 25 mg, the samples were dried in vacuum. DSC scans were recorded during heating, cooling and second heating in the temperature range from -100 ^oC to 250 ^oC at heating rate of 10 ^oC/min under nitrogen atmosphere.

— The hydroxyl number was determined by standard titration (PN-90/C-89406) and calculated from three measurements and averaged.

— For hydrolytic degradation, the weighted discs (0.115 g) were placed in the dishes containing 2 ml phosphate buffered saline (PBS, pH 7.2) and Hydrion solution (pH 5.0 and 9.0), maintained in thermostatically controlled chamber at 37 ^oC. The discs were removed from the buffers every week. The films were dried under vacuum at 30 ^oC to constant weight. The weight loss was calculated by comparing the initial mass (W_0) with the mass measured after a given time (W_t), as shown in Equation (1).

$$\text{Weight loss } (WL, \%) = [(W_t - W_0)/W_0] \cdot 100 \qquad (1)$$

Three individual experiments were performed for degradation test, and then the average value was calculated.

— Mechanical properties were investigated using the samples in the shape of B5 dumbbells (parallel length 20 mm and cross-section 2 mm^2). They were tested using Instron 1161 testing machine equipped with a 500 N load cell at a crosshead speed of 100 mm/min according to PN-EN ISO 527-1. Strain at break of tested material was taken as the total clamp displacement.

RESULTS AND DISCUSSION

Series of new poly(ester-carbonate-urethane) copolymers with variable concentration of ester and carbonate units was prepared.

Table 1. Molecular weights and molar mass dispersity of selected poly(ester-carbonate-urethane)s

PTMCD, wt. %	DD, wt. %	M_n	M_w	*DM*
70	30	50 473	129 271	2.56
50	50	40 891	124 263	3.04
30	70	35 069	88 046	2.51

The molecular weights and molar mass dispersity (*DM*) values of selected products are given in Table 1.

Chemical structure

ATR FT-IR spectra of PTMCD showed the absorption band at 3600—3400 cm^{-1} corresponding to hydroxyl groups occurring at the ends of PTMCD backbone chain. The absorption bands at 2967 and 2907 cm^{-1} are associated with symmetric and asymmetric methylene groups. The strong signal at 1733 cm^{-1} was assigned to -C=O from carbonate group. The ester absorption band, corresponding to vibration of C-O band occurred at 1230 cm^{-1} (spectra not showed in this paper).

^{1}H NMR spectra of PTMCD (Fig. 1) showed four characteristic peaks at: δ a 3.7 ($-CH_2-OH$), δ b, d 2.1; 1.8 ($-CH_2-$), δ c 4.3; 4.2 ($-CH_2-O-$). From the intensity ratio of terminal CH_2 groups and those adjacent to the carbonate linkages it was calculated that molecular weight of oligocarbonate was 1278 g/mol, what is in a good agreement with L_{OH} data (1316 g/mol) (M_n value from GPC was almost two times higher due to the problems with separation on the columns used).

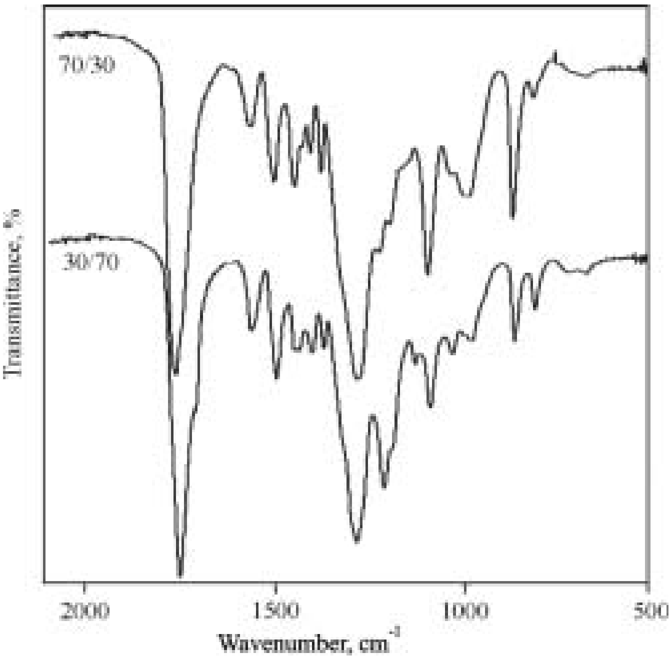


Fig. 2. ATR FT-IR spectra of poly(ester-carbonate-urethane)s

ATR FT-IR spectra of selected poly(ester-carbonate-urethane) copolymers next to the fingerprint region are shown in Fig. 2. In general, all characteristic absorption bands confirming chemical structure were detected. The absorption at higher wave numbers, *i.e.* at 3300—3500 cm^{-1}, corresponds to stretching vibrations of N-H groups. The absorption bands at 2967 and 2907 cm^{-1} associated with symmetric and asymmetric methylene groups were also identified. The strong band at 1700 cm^{-1} shown in Fig. 2 is assigned to the -C=O groups. The bands centered within 1500—1550 cm^{-1} correspond to deformation vibrations of N-H groups in urethane formations. The bands at 1200—1000 cm^{-1} are

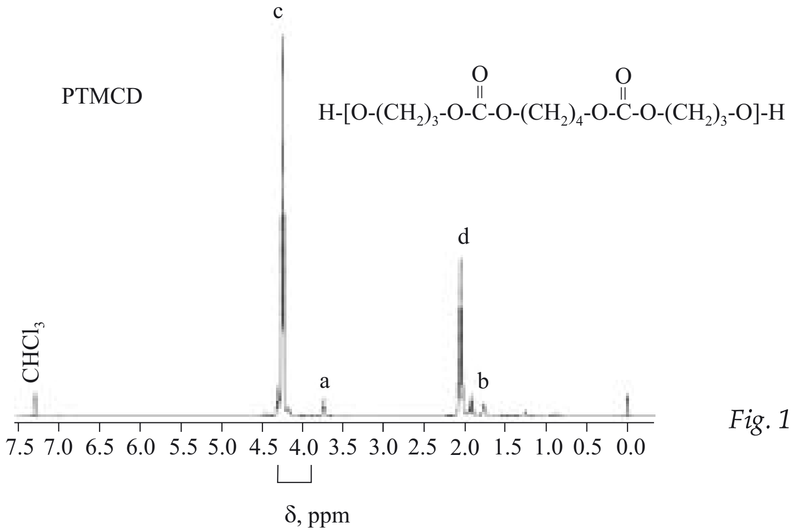


Fig. 1. ^{1}H NMR spectrum of PTMCD

assigned to the stretching vibration of the ester group and the band at 700 cm^{-1} is assigned to the out-of-plane bending of the ester group. Different contents of carbonate/ester units resulted in different absorption bands intensities in IR spectra, especially at 300 cm^{-1}, 3300 cm^{-1}, 1200 cm^{-1}, and 700 cm^{-1}.

So, the IR and ^{1}H NMR spectra of PTMCD and new poly(ester-carbonate-urethane)s confirm the chemical structures of these products.

Thermal characteristics

DSC measurements confirmed the random structures of synthesized copolymers since they exhibited transition temperatures between those of the corresponding homopolymers (Figs. 3 and 4). The typical values of the temperature phase transitions of homopolymers and copolymers are summarized in Table 2. The DSC analysis shows strong correlation between characteristic temperature transitions and polymer composition.

The thermograms from second heating (Fig. 3) showed that the values of glass transition (T_g) were between those of DD (-77 °C) and PTMCD (-35 °C), and T_g shifts to higher temperature with increasing concentration of PTMCD (and none of the samples showed two separate transitions, thus confirming the random structures of copolymers). Incorporation of ≥50 wt. % DD units into copolymer structure leads to appearance of melting point (T_m) of polymers (samples 4—6), reflecting incorporation of a semicrystalline DD into polymer structure. Moreover, these samples showed "cold crystallization" (designated as T_{c*}) due to the fact that amorphous (PTMCD) and semicrystalline (DD) phases are mixed.

Table 2. Thermal transitions data of PTMCD, DD and copolymers[*)]

Sample	PTMCD wt. %	DD wt. %	T_g °C	ΔC_p J/g·°C	T_m °C	ΔH_m J/g	T_c °C	ΔH_c J/g
1	100	0	-35.0	0.607	—	—	—	—
2	70	30	-39.8	0.399	—	—	—	—
3	60	40	-43.9	0.528	—	—	—	—
4	50	50	-54.7	0.401	10.5	9.40	-22.7	2.49
5	40	60	-55.1	0.222	15.5	11.50	-20.6	0.08
6	30	70	-56.0	0.274	17.9	16.90	-19.3	0.13
7	0	100	-77.3	0.229	26.1	35.13	3.7	47.16

[*)] T_g — glass transition temperature, °C; ΔC_p — heat capacity, J/g · °C; T_m — melting point, °C; ΔH_m — heat of fusion, J/g; T_c — crystallization temperature, °C, ΔH_c — heat of crystallization.

The cooling curves (Fig. 4) show low temperature crystallization exotherms for copolymers with DD content higher than 50 wt. % (samples 4—6 in Table 2), and a very strong crystallization peak for DD. The intensity of this exotherm is decreasing with increasing concentration of amorphous PTMCD content up to 60 wt. %, where crystallization was not detected. Therefore, the materials containing more than 50 wt. % of DD units are semicrystalline, whereas these with lower DD content are amorphous. Similar behavior was observed for P(TMC-*co*-CL) prepared by Schappacher and coworkers

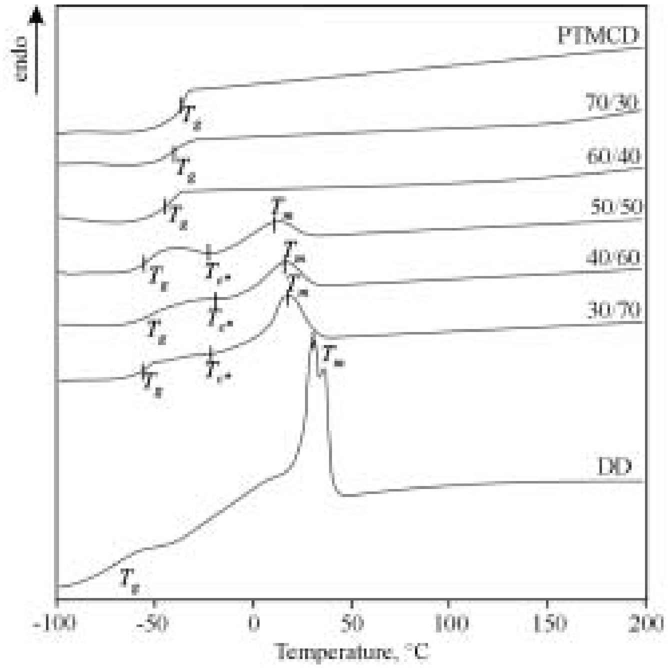


Fig. 3. DSC thermograms of PTMCD, DD and copolymers from second scanning run; heating rate 10 °C/min (symbols of transition temperatures — see footnote to Table 2; T_{c*} — "cold cristallization")

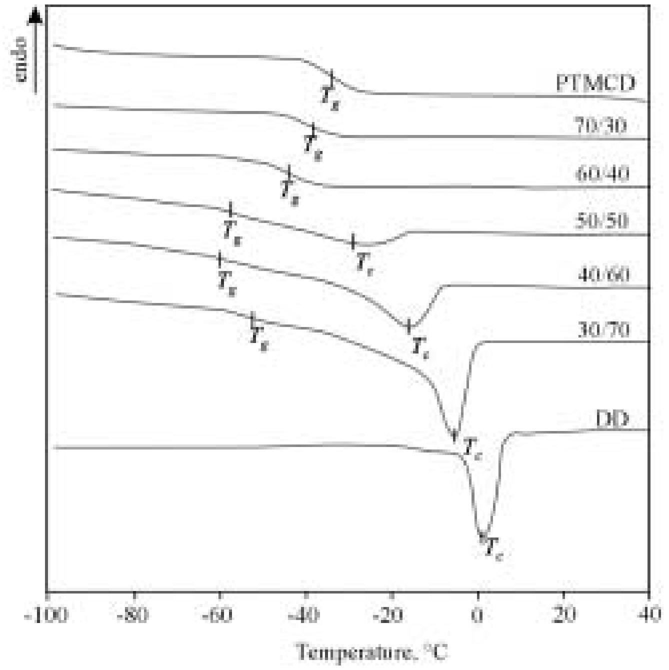


Fig. 4. DSC thermograms of PTMCD, DD and copolymers from the cooling run

[28]: at high TMC content (>80 wt. %) copolymers were amorphous while at lower concentration — semicrystalline.

Mechanical properties

Table 3 summarizes mechanical properties of poly(ester-carbonate-urethane) copolymers. Dependently on the carbonate/ester units content, mechanical behavior is changing from weak and brittle material (sample 2) to mechanically stable and elastic one (sample 6). Materials containing more than 50 wt. % of ester units (samples 4—6), showed higher than 100 % elongation at break.

Table 3. Mechanical properties of poly(ester-carbonate-urethane) copolymers

Sample*)	Tensile strength σ, MPa	Elongation at break ε, %
2	0.47 ± 0.08	27.8 ± 3.3
3	0.76 ± 0.06	60.7 ± 11.6
4	1.23 ± 0.19	148.2 ± 7.4
5	1.33 ± 0.24	160.5 ± 32.8
6	1.73 ± 0.14	331.9 ± 25.1

*) Compositions — see Table 2.

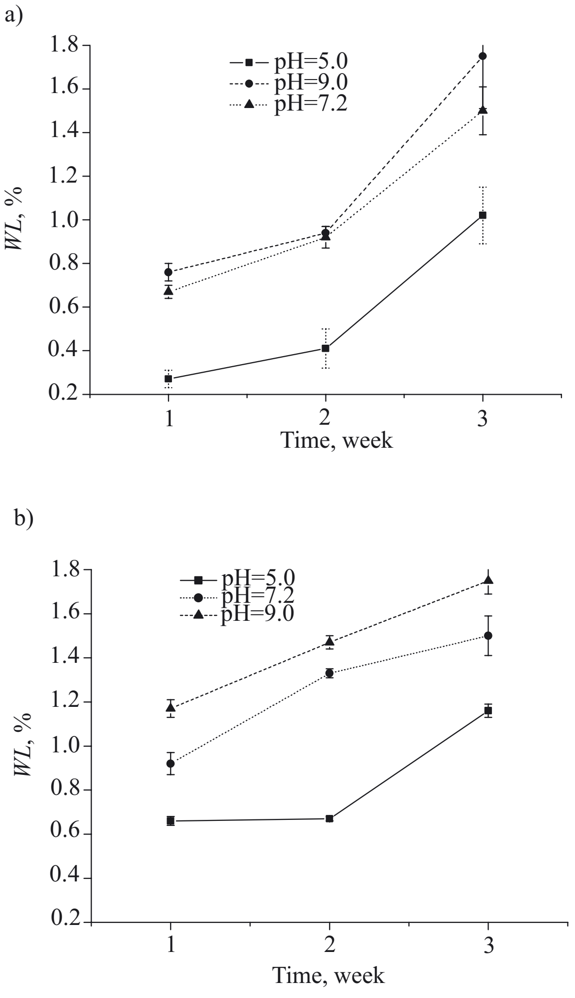


Fig. 5. Weight loss (WL) during hydrolytic degradation of materials containing 60 wt. % (a, sample 3) or 50 wt. % (b, sample 4) carbonate units at different pH

Hydrolytic degradation

As it was mentioned, short term hydrolytic degradation of materials was investigated by monitoring the weight loss changes during the degradation in PBS and Hydrion buffer at pH 7.2, pH 5.0 and pH 9.0, respectively. Measurements were conducted for samples 3 and 4 (containing 50 and 60 wt. % of carbonate units, respectively). The degradation process showed up to 1.8 % weight loss after three weeks of degradation (Figs. 5a, b).

The weight loss was lower at pH 5.0 and higher at pH 9.0. Faster course of weight loss at pH 9.0 can be explained by the fact that the base environment promotes hydrolysis of esters bonds occurring in material in the presence of strongly nucleophilic OH^- reagent [23]. Larger weight loss was observed for sample 3 (60 wt. % of carbonate units) which demonstrated worse mechanical properties (Table 3) as compared to the sample 4 (50 wt. % of carbonate units). Small values of *WL* for both samples showed, however, that despite of introduction of hydrophobic ester units into copolymers structures, their degradation times could be adjusted by appropriate carbonate/ester units concentration.

Final verification of susceptibility of these materials to biodegradation (in biologically active environment) will be reported in a separate paper.

CONCLUSIONS

It was showed that TMC-based copolymers were successfully prepared by coupling of polyester and polycarbonate diols using diisocyanate. A series of poly(ester-carbonate-urethane)s containing different block concentrations were synthesized. Thermal properties as well as mechanical behavior can be controlled by monomers concentrations on the feed. Polymers are susceptible to degradation at various pH values in the range 5.0—9.0 but show rather small weight loss after three weeks of degradation in these conditions. For selected samples, however, faster degradation was observed at pH 9.0 in comparison to neutral or acidic environments.

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