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Fibre-grade copoly(oxyethylene-*b*-ethylene terephthalate)s with improved optical properties

RAPID COMMUNICATION

Summary — The conditions of synthesis of block copoly(oxyethylene-*b*-ethylene terephthalate)s (PEG-*b*-PET) with good optical parameters and designed for the production of hydrophilic fibers are presented. For polycondensation the catalysts: antimony trioxide (Sb_2O_3) and titanium tetraisopropoxide [Ti(O*i*Pr)$_4$] were used. The best optical properties of the polymers were achieved by using the mixture of Sb_2O_3/Ti(O*i*Pr)$_4$ catalysts. The system which thermally stabilize the PEG-*b*-PET copolymers was selected. It was stated that the melting temperature (T_m) of the copolymer was insignificantly lower than that of the PET homopolymer (ΔT = 11 K) when the content of PEG 4000 comonomer amounts 30 wt. %. When the weight fraction of PEG 4000 in the copolymer does not exceed 20 wt. % a cold crystallization is observed.

Keywords: poly(ether-*b*-ester), poly(ethylene terephthalate), stabilization, thermo-oxidative degradation.

WŁÓKNOTWÓRCZE KOPOLI(OKSYETYLENO-*b*-ETYLENOTEREFTALANY) O POLEPSZONYCH WŁAŚCIWOŚCIACH OPTYCZNYCH

Streszczenie — Przedstawiono warunki syntezy blokowych kopoli(oksyetyleno-*b*-etylenotereftalanów) (PEG-*b*-PET) o dobrych parametrach barwy, przeznaczonych do produkcji włókien hydrofilowych. Do polikondensacji zastosowano katalizatory tritlenek antymonu (Sb_2O_3) oraz tetraizopropoksytytan [Ti(O*i*Pr)$_4$]. Najlepsze parametry barwy uzyskano stosując mieszaninę katalizatorów Sb_2O_3/Ti(O*i*Pr)$_4$. Wytypowano układ stabilizujący termicznie kopolimery PEG-*b*-PET. Stwierdzono, że przy zawartości 30 % mas. komonomeru PEG 4000 temperatura topnienia PEG 4000-*b*-PET jest nieznacznie niższa od homopolimeru PET (ΔT = 11 K). Zauważono występowanie zimnej krystalizacji w kopolimerach PEG-*b*-PET o zawartości nie większej niż 20 % mas. komonomeru.

Słowa kluczowe: poli(etero-*b*-estry), poli(tereftalan etylenu), stabilizacja, degradacja termo-oksydacyjna.

Copoly(oxyethylene-*b*-ethylene terephthalate)s (PEG-*b*-PET)s are classified into a group of the thermoplastic elastomers, because the macromolecules of these polyesters are composed of two kinds of blocks: soft polyether and hard polyester segments. The flexibility of the material arises from the blocks obtained from poly(oxyethylene)diol (PEG) because they exhibit low glass transition temperature (T_g) [1—4]. In the recent years, the PEG-*b*-PET copolymers have found the application as the hydrophilic fibers. These fibers being manufactured in the form of staple and filament fibers exhibit special breathing and soft properties [5]. The synthesis of block copoly(oxyethylene-*b*-ethylene terephthalate) in melt requires an appropriate thermal stabilization because poly(oxyethylene)diol is thermally unstable, and its thermal destruction proceeding at temperature above 200 °C causes the yellowing effect of polymer [6—9].

EXPERIMENTAL

Materials

Dimethyl ester of terephthalic acid (DMT, Boryszew SA Elana Branch in Toruń, Poland), ethylene glycol (EG, Orlen, Poland), poly(oxyethylene)diol characterized with the molecular weight of 4000 (PEG 4000, Sasol), pentaerythritol (Boryszew SA Elana Branch in Toruń, Poland) as a branching agent, monoglycol ester of phosphoric acid (GEPA, Boryszew SA, Poland) as a metal scavenger of the ester exchange catalysts, were all used as received.

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The following catalysts were used: manganese acetate, cobalt acetate, antimony trioxide (Sb_2O_3) (all from Boryszew SA Elana Branch in Toruń), and titanium tetraisopropoxide (TPT, DuPont de Nemours).

Thermal stabilizers Irganox 1010 and Irganox HP 2921 FF were kindly donated by Ciba Specialty Chemicals.

Preparation of poly(ether-*b*-ester) copolymers

The syntheses were performed by a three-stage batch method using the two reactors system. Stage I comprises the synthesis of bis-(β-hydroxyethylene terephthalate) (BHET) basing on the transesterification of DMT by ethylene glycol (EG). Transesterification reactor was charged with 569.6 g of DMT and 364.1 g of ethylene glycol. Simultaneously with DMT, pentaerythritol in the amount of 0.14 wt. % (per weight of DMT) was added. As the transesterification catalysts manganese acetate in the amount of 0.03 wt. % (per weight of DMT) or cobalt acetate in the amount of 0.01 wt. % (per weight of DMT) were used. The reactor was heated at the temperature range 160—220 °C for 2 h with methanol removed as the reaction by-product and distillation of unreacted amounts of EG. At the end of the transesterification stage GEPA was introduced into the reaction medium with the molar ratio of phosphorus and manganese and cobalt P/Mn, Co = 1 and/or with ratio of phosphorus and manganese, cobalt and titanium P/Mn, Co, Ti = 1. After this operation, obtained BHET and 239.8 g of PEG 4000 was charged into polycondensation reactor. Together with PEG 4000, Irganox 1010 in the amount of 0.10 wt. % (per weight of DMT and EG) and Irganox HP 2921 FF in the amount of 0.32 wt. % (per weight of polymer) were added. Stage II is polycondensation of BHET and PEG 4000 to obtain a prepolymer, and it was carried out under reduced pressure, termed as the preliminary polycondensation process.

Table 1. Composition of prepared PEG-*b*-PET copolyesters samples and intrinsic viscosity [η]

Symbol of sample	PEG 4000 content wt. %	Polycondensation catalyst	η, dl/g
P-0	0	Sb_2O_3	0.640
P-1	10	Sb_2O_3	0.674
P-2	14	Sb_2O_3	0.845
P-3	20	Sb_2O_3	0.786
P-4	24	Sb_2O_3	0.846
P-5	30	Sb_2O_3	0.890
P-6	36	Sb_2O_3	1.080
P-7	30	Sb_2O_3 / TPT	0.909

Stage III is the polycondensation of prepolymer carried out under pressure below 80 Pa in the presence of Sb_2O_3 in the amount of 0.04 wt. % (per weight of DMT) or Sb_2O_3 in the amount of 0.04 wt. % with TPT in the amount of 0.02 wt. % (per weight of DMT) as a co-catalyst. The polycondensation temperature was maintained in the range 255—265 °C for 2 h and 800 g of the copolyester containing 30 wt. % of oligoether fragments was obtained.

There were obtained the PEG-*b*-PET copolymers (Table 1) in which the content of PEG 4000 were variable.

Methods of testing

The intrinsic viscosity [η] was examined according to the standards ISO 1628-1 and ISO 1628-5.

The measurement of acetaldehyde content (C_{AA}) bases on an analysis of the gas phase obtained from polymer sample by chromatographic method.

The measurement of thermal parameters was performed using an instrument DSC 200 ASC (Netzsch), at the heating rate 20 deg/min in the temperature range 25—300 °C.

The content of carboxylic groups (COOH) was examined by titration of a polymer solution with alcoholic solution of KOH in the presence of phenol red.

The measurement of colour was performed by spectroscopic method according to standard ASTM D42244. This method based on the determination of brightness (L*), green-red shade (a*) and blue-yellow shade (b*) in accordance with the CIELab international system of color specification of the three values by means of computer system for color determination. The most essential criterion to evaluate the polymer color is yellowing parameter (b*). When the parameter b* takes the positive values the polymer color takes a yellow shade. The higher is a value of this parameter, the more intensive is the coloration. It is preferred that the b* value does not exceed +10, because above this value, the yellow colour becomes intensive enough, to be noticeable in thin-walled products. The parameter a* is also important. It is assumed that the polymer has the best color when the value of this parameter fluctuates near zero or takes the negative numbers, but not smaller than -5. Polymer lightness is determined by the parameter L*, the higher is L* the better is lightness of the polymer.

RESULTS AND DISCUSSIONS

The DSC diagram of the PEG-*b*-PET copolymers presented in Figure 1 shows characteristic transition temperatures. The values of melting temperature (T_m) heat of melting (ΔH_m), two crystallization temperatures corresponding to first heating and second cooling (T_{c1} and T_{c2}, respectively), two crystallization enthalpy values (ΔH_{c1} and ΔH_{c2}) and glass transition temperature (T_g) for all prepared samples are listed in Table 2. With an increase in the fraction of oligoether blocks in the range 0—30 wt. % values of T_m and (ΔH_m) of the copolymers decrease insignificantly. This is specially valid for T_m de-

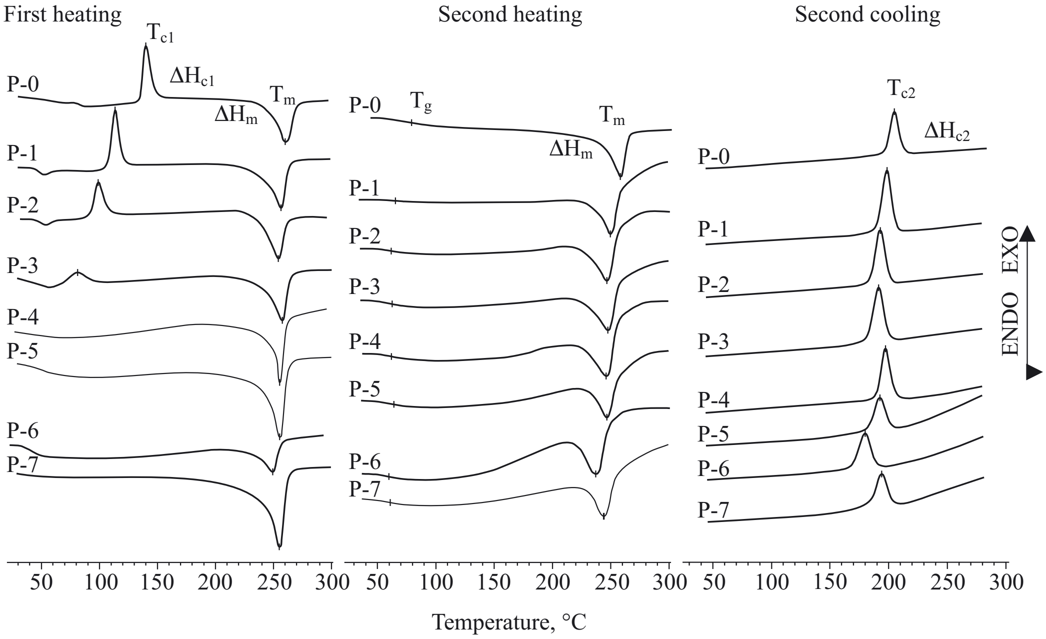

Fig. 1. DSC thermograms of PEG-b-PET copolymers and PET polymer

T a b l e 2. Thermal properties of PEG-*b*-PET copolymers

Symbol of sample	First heating			Second heating			Second cooling	
	T_m °C	T_{c1} °C	ΔH_{c1} J/g	T_m °C	ΔH_m J/g	T_g °C	T_{c2} °C	ΔH_{c2} J/g
P-0	260	140	31	258	45	82	205	51
P-1	256	112	24	250	57	64	198	49
P-2	255	98	19	247	61	61	194	44
P-3	257	81	11	247	61	60	191	42
P-4	256			245	60	62	197	40
P-5	255			247	52	65	194	33
P-6	250			236	46	60	180	30
P-7	255			245	55	62	193	32

termined in the first heating cycle. T_m decreases in a visible way for sample P-6 with 36 wt. % fraction of PEG. This results from the long PET sequences which can be obtained by using the PEG blocks of the molecular weight equal 4000 g/mol. This disables the miscibility of these blocks, hence facilitates the phase separation and formation of nondefective crystalline phase. In the copolymers with shorter PET sequences (*e.g.* with PEG 1000 g/mol) the small molecular fractions of these blocks may be miscible among themselves causing defecting of the crystal lattice [3]. Similarly as T_m, the crystallization temperature (T_{c2}) decreases visibly for sample P-6 (36 wt. % fraction of PEG 4000 in the copolymer). In contrary to ΔH_m, the value of ΔH_{c1} and ΔH_{c2} decrease with an increase in the ether fragments' content. It is a rule, that T_g values of the block polymers decrease with an increase in the soft blocks content. In the PEG-*b*-PET copolymers, the fraction of PEG 4000 in the studied range of content 0—40 wt. % has only an insignificant influence on T_g. In such ether-ester block copolymers an intrinsic viscosity (η) increases with an increase in the ether fragments' content in the copolymer.

T a b l e 3. Effects of thermal stabilizer and catalytic system on C_{AA}, content of COOH groups and optical parameters of PEG-*b*-PET copolymers

Sample	C_{AA} ppm	[COOH] [mval/kg]	L*	a*	b*	Color
P-5	20	9.2	67.4	+0.1	10.3	light-yellow
P-7	27	8.9	70.6	-2.0	4.0	light, colorless

The mechanical properties of the PEG-*b*-PET materials vary significantly with the content of the oligoether moieties in the polymer chain. As the fraction of PEG increases, the polymer changes from brittle to flexible. The direct reason of this phenomenon is related with low crystallization peak at T_{c1} and described as primary crystallization effect in which the imperfect crystalline phase is forming with low density poorly developed crystals [10]. As it can be seen from Table 2 the copolymer containing 14 wt. % of the oligoether fragments (P-2) exhibits T_{c1} slightly below 100 °C and it is a flexible material. For lower content of the oligoether fragments (P-1), when T_{c1} is higher than 100 °C, the polymer becomes brittle and breakable. Those materials after processing do not become flexible but they are still brittle and breakable, because the same described primary crystallization takes place.

Optical properties of samples P-5 and P-7 are listed in table 3. Good results in reduction of yellow color saturation in the obtained copolymers were achieved by use of Irganox 1010 and Irganox HP 2921 FF mixture (Table 3).

When the catalytic system Sb_2O_3/TPT was used in the polycondensation (sample P-7), the copolymer showing the best L*, a* and b* parameters was obtained. The TPT catalyst accelerated the polycondensation and enabled to obtain the copolymer with a larger molecular weight. The acetaldehyde content in the copolymer for synthesis of which TPT catalyst was used (sample P-7), is higher than that in the sample P-5 copolymer. This resulted from the fact that titanium catalysts such as TPT are forming titanium compounds with vinyl groups by dehydroxylation. Vinyl groups favour the formation of the peroxy radicals [$ROO^\bullet$] initiating the formation of acetaldehyde [10]. The slightly lower content of carboxylic groups in copolymer P-7 than in copolymer P-5 is correlated with higher molecular weight of this polyester.

CONCLUSIONS

The introduction of PEG 4000 comonomer to the PET macromolecule in the amount not larger than 30 wt. % does not influence significantly T_m value of this polymer and the copolymers with PEG content below 14 wt. % of the oligoethers fragments are brittle and unfit for processing. The problem with thermal instability of obtained materials under the polycondensation conditions was solved by the addition of a mixture of Irganox HP 2921 FF with Irganox 1010. The introduction of TPT as the co-catalyst enabled to obtain the copolymers having a high intrinsic viscosity and white color.

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