

Synthesis and characterization of thermoplastic copolyester elastomers modified with fumaric moieties

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A series of poly(ether-ester)s derived from dimethyl terephthalate (DMT), dimethyl fumarate (DMF), 1,4-butanediol (BD) and poly(tetramethylene oxide) (PTMO, $\bar{M}_n = 1000$ g/mol) was synthesized in a two stage process involving transesterification and polycondensation in the melt. The mole ratio of the starting components was selected to result in copolymers with a constant hard:soft segment weight ratio (56:44). The amount of DMF was 10 mol %, referred to the total amount of the esters used. The synthesis was optimized in terms of both the concentration of catalyst, tetra-*n*-butyl-titanate, $\text{Ti}(\text{O}i\text{Bu})_4$ and thermal stabilizer *N,N'*-diphenyl-*p*-phenylenediamine, DPPD, as well as the temperature. The composition and structure of the synthesized poly(ether-ester)s were characterized by $^1\text{H-NMR}$. The number average molecular weights of the polymers calculated from the $^1\text{H-NMR}$ spectra were compared with the corresponding values of the inherent viscosity (η_{inh}) in *m*-cresol and the complex dynamic viscosity (η^*). The effect of the content of fumaric residues on the thermal properties of the synthesized copolyesters was also investigated using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

Keywords: thermoplastic elastomers, poly(ether-ester)s, fumaric residue, $^1\text{H-NMR}$ -spectroscopy.

INTRODUCTION

Thermoplastic elastomers have found wide application thanks to their excellent mechanical and physical properties. They behave as elastomers at ambient temperatures, but are thermoplastic at elevated temperatures when they can be molded and remolded. These polymers exhibit mechanical properties of chemically crosslinked elastomers, like for example: reversible elasticity, great impact strength and good flexibility at low temperatures.

In addition, they have an important practical advantage over conventional elastomers in that there is no need for an additional chemical crosslinking reaction. Also, unlike conventional elastomers, these materials can be processed by injection, compression, transfer and blow molding, extrusion and calendering.¹ Typical examples of ther-

moplastic elastomers are styrene-diene triblock copolymers, block copolyurethanes, block copoly(ether-amide)s and block copoly(ether-ester)s.

The thermoplastic and elastic behaviour of these polymers is due to the existence of two types of segments in the macromolecules, hard and soft. It is generally assumed that the soft phase is responsible for the reversible elasticity of the polymeric material, whereas the hard phase is responsible for the mechanical strength properties. The properties of thermoplastic elastomers depend on many variables, such as the chemical structure of each segment, the molecular weight of the soft segment, the hard/soft segment content ratio and, in some cases, soft-segment crystallization and the ability to form discrete glassy or crystalline and rubbery microdomains. In the case of block copoly(ether-ester)s, the hard segment is often a semicrystalline polyester, which is made by the reaction of a low molecular weight diol with a dicarboxylic acid. These segments are organized into domains which act as physical crosslinks. They can undergo some kind of intermolecular association with other hard blocks thereby forming physical crosslinks which provide dimensional stability and minimize cold flow. While, the soft segments in the polymer chain refer to the reaction product of a long chain glycol with dicarboxylic acids. These segments act as a rubber matrix, which has a relatively low glass transition temperature. The thermodynamic immiscibility of the hard and soft segments at low temperatures results in phase separation and, consequently, in a domain structure. The existence of a two-phase structure in these polymer, which is the result of crystalline and amorphous domains, was shown and confirmed by thermal analysis and electron microscopy.¹⁻⁴

The application of thermoplastic poly(ether-ester)s include motor vehicle parts, flexible joints, cabling, and hosing, as well as impact and sound absorbing devices.

Thermoplastic poly(ether-ester) elastomers are random copolyesters of terephthalic acid and 1,4-butane diol and low molecular weight poly(tetramethylene oxide). These copolyesters are prepared by melt transesterification. Details of the synthesis as well as problems relating to the stabilization of the polymers have been described by Witsiepe, Hoeschele *et al.*⁵⁻⁷ These polymers are commercially available from E. I. du Pont de Nemours under the trademark "Hytrel" polyester elastomers and from Akzo Plastics as "Arnitel". Commercial poly(ether-ester)s generally contain poly(butylene terephthalate) (PBT) as the hard block and poly(ethylene oxide), poly(1,2-propylene oxide) or poly(tetramethylene oxide) (PTMO) as the soft block. Some modifications with isophthalic acid or phthalic acid were used in order to optimize the mechanical properties. Poly(ether-ester)s based on PBT and poly(ethylene oxide) (PEO)⁸⁻¹⁰ have been shown to have generally worse characteristics than those containing PTMO as the soft segments, but also to have some advantages, the most important being their hydrophilic character, which makes them attractive candidates for application in the textile industry. The resistance to hydrolytic and thermal degradation increased when poly(hexamethylene oxide) and poly(decamethylene oxide) were introduced as the soft segments.¹¹ There have been reports that unsaturated units were incorporated into the copolyester backbone, in order to obtain thermoplastic elastomers with lower flammability and increased oxygen index and char formation.^{12,13}

In this paper, the use of fumaric acid derivatives in the copolyester synthesis which enables the introduction of unsaturated reactive sites into the polymer chain is presented. The introduction of these reactive double bonds into the main chain allows the polymer to be subsequently crosslinked which would result in a diminished cold flow and an improvement of some other mechanical and thermal properties of poly(ether-ester)s modified with fumaric acid residues. It has also been reported that the introduction of double bonds into some copolyesters results in the polymer having fiber-forming properties¹⁴ and gives the opportunity of reaction with the polyester matrix in composites. The *trans* double bond from fumaric acid is very reactive due to the adjacent carbonyl group, which permits ready crosslinking but requires control over the polymer synthesis and an understanding of the effect of the polymer structure on its physical properties and thermal degradation.

In this paper, preliminary results on the synthesis and characterization of these novel thermoplastic poly(ether-ester)s modified with 10 mol % of fumaric acid will be discussed. The effect of the catalyst $\text{Ti}(\text{O}i\text{Bu})_4$ and thermal stabilizer *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) concentration, as well as the temperature on the molecular weight of the poly(ether-ester)s were investigated in order to determine the optimum conditions for the preparation of copolymers based on fumaric acid.

EXPERIMENTAL

Reagents

Poly(tetramethylene oxide), PTMO (from Merck), with molecular weight of 1000 g/mol was used as obtained. Dimethyl terephthalate, DMT, was recrystallized from absolute ethanol. 1,4-Butanediol (from Fluka) was purified by vacuum distillation. Dimethyl fumarate, DMF (from Aldrich), was used as obtained. Tetra *n*-butyl titanate, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (from Aldrich), was used as a solution in dry *n*-butanol (1:9 vol.). *N,N'*-Diphenyl-*p*-phenylenediamine, DPPD (from Bayer), was used without any further purification.

Synthesis

The poly(ester-ether)s were synthesized by a two-step catalyzed melt transesterification. A typical experiment was performed as follows: poly(tetramethylene oxide) (0.020 mol), anhydrous 1,4-butanediol (0.198 mol), dimethyl terephthalate (0.140 mol) and dimethyl fumarate (0.015 mol) were added to a 250-ml glass flask equipped with a thermometer, magnetic stirrer, nitrogen inlet tube, and a distillation head connected to a condenser. The excess of the hydroxyl groups relative to the carboxylic groups was 45 mol % in all reaction mixtures. The reaction mixture was heated on a silicone oil bath under a nitrogen atmosphere.

The first step, *i.e.*, transesterification, was carried out at 160 °C. The reaction mixture was maintained at 160 °C for five minutes and then the solution of catalyst was added (1.5 or 2.0 mmol/mol ester) whereupon, methanol distilled immediately from the reaction mixture. The temperature of the reaction mixture increased during one hour to its maximal value. After the first step, the volume of methanol was measured and then thermal stabilizer DPPD was added (1 wt.-%) to the reaction mixture and the pressure reduced slowly.

The second step, *i.e.*, polycondensation, was carried out by heating the reaction mixture at the maximal temperature, and under vacuum (< 1 mm Hg) to remove the excess 1,4-butanediol. The end of synthesis was signaled by a rapid increase in the viscosity of the reaction mixture. The viscous slurry was cooled in the reactor under nitrogen, and then it was pulled from the reactor.

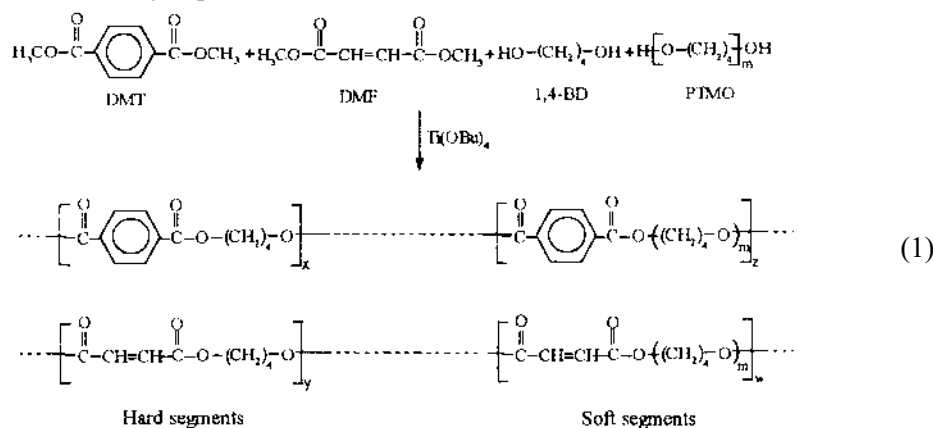
Characterization

The composition and molecular weight of the copolyesters were determined by $^1\text{H-NMR}$ (Varian-GEMINI 200 MHz) using solutions in CDCl_3 with tetramethylsilane (TMS) as the internal standard. The inherent viscosity, η_{inh} of the polymers were determined in *m*-cresol solution (0.5 g/dl) at 30–0.5 °C using an Ostwald capillary viscometer. The complex dynamic viscosity (η^*) of the polymer melts were recorded with a Rheometrics mechanical spectrometer RMS-605 operating in the dynamic shear mode between parallel plates, at 220 °C. The frequency was varied from 0.1 to 100 rad/s. The plate diameter was 25 mm, and the gap between the plates about 1.0 mm. The glass transition temperatures were determined using a Perkin Elmer Thermomechanical analyzer TMS-2 in the temperature range –40 to 20 °C at a heating rate of 5 °C/min. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer DSC-2. The samples of the poly(ether-ester)s were analyzed under a nitrogen atmosphere in the temperature range 50 to 250 °C at a heating rate of 10 °C/min and cooling rate of 40 °C/min. The TGA curves of the copolyesters were obtained using a Perkin-Elmer TGS-2 at a heating rate of 10 °C/min in either an O_2 or N_2 atmosphere (flow rate of 20 ml/min).

RESULTS AND DISCUSSION

A series of thermoplastic poly(ether-ester)s modified with 10 mol % of fumaric moieties were synthesized by a two step bulk polycondensation. The first step, *i.e.*, transesterification, was carried out at normal pressure in the presence of a transition metal complex with a 40 % stoichiometric excess of hydroxyl groups. For the second step, *i.e.*, bulk polycondensation, thermal stabilizer, *N,N'*-diphenyl-*p*-phenylenediamine, DPPD was added and the reaction was carried out under vacuum to remove the excess glycol and hence produce chain extension.

The reaction scheme for the synthesis poly(ether-ester)s modified with fumaric acid is shown by Eq. (1).



Optimization of the synthesis of poly(ether-ester)s

In previous investigations it was found that poly(ether-ester)s could be effectively stabilized by the addition of a suitable thermal stabilizer, such as *N*-isopropyl-*N'*-diphenyl-*p*-phenylenediamine (IPPD) or *N,N'*-diphenyl-*p*-phenylenediamine (DPPD). The later one was particularly effective as the copolyester had higher molecular weights when prepared in the presence of this thermal stabilizer and $\text{Ti}(\text{OBu})_4$ as catalyst.¹⁵

TABLE I. Condition of synthesis and viscosity of poly(ether-ester)s modified with fumaric acid

Sample	Catalyst mmol/mol ester	Thermal stabilizer wt. %	Temper. °C	Time II phase min	inh dl/g	* Pas
TPE-1	1.5	0.24	250	30	0.336	64.9
TPE-2	1.5	0.53	250	90	0.573	72.9
TPE-3	1.5	0.24	230	120	0.471	41.1
TPE-4	1.5	0.24	230	180	0.565	68.1
TPE-5	2.0	0.24	230	75	0.572	74.0
TPE-6	2.0	0.67	230	330	0.710	89.4
TPE-7	2.0	1.0	230	180	0.758	446
TPE-8	2.0	1.0	220	420	0.614	70.0
TPE-9	2.0	1.0	230	450	0.752	341

In this work, the effects of the concentration of the catalyst, tetra-*n*-butyl-titanate ($\text{Ti}(\text{OBU})_4$) (1.5–2.0 mmol/mol ester) and the thermal stabilizer *N,N'*-diphenyl-*p*-phenylenediamine, DPPD (0.24 wt. % to 1.0 wt. %), as well as the temperature on the formation of the poly(ether-ester)s were investigated. The formation of the poly(ether-ester)s was monitored by measuring the inherent and complex dynamic melt viscosities of the obtained polymers. The results are presented in Table I and Figs. 1. and 2.

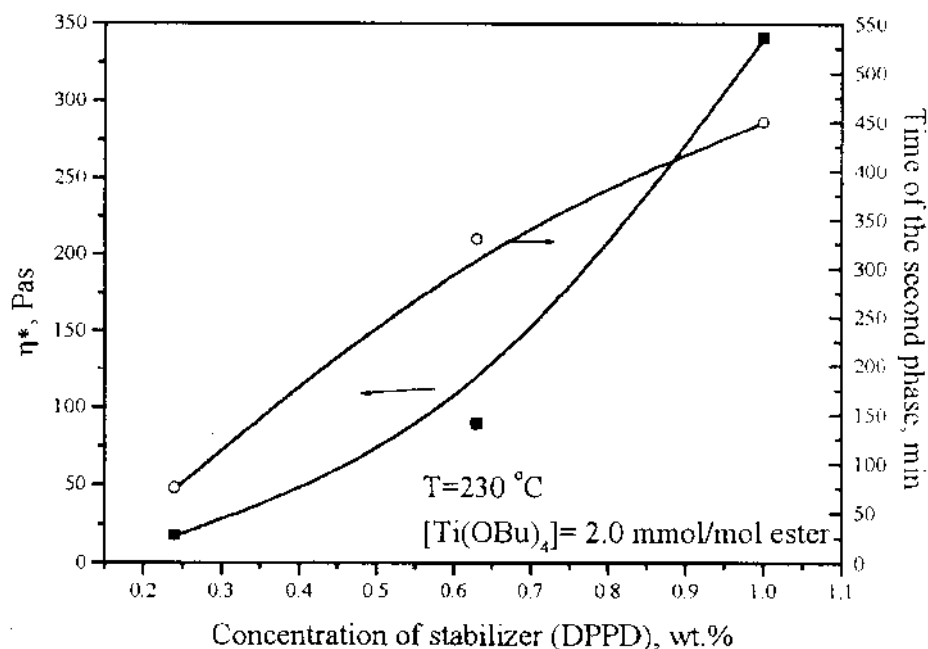


Fig. 1. Effect of thermal stabilizer (DPPD) concentration on the complex dynamic viscosity and re-

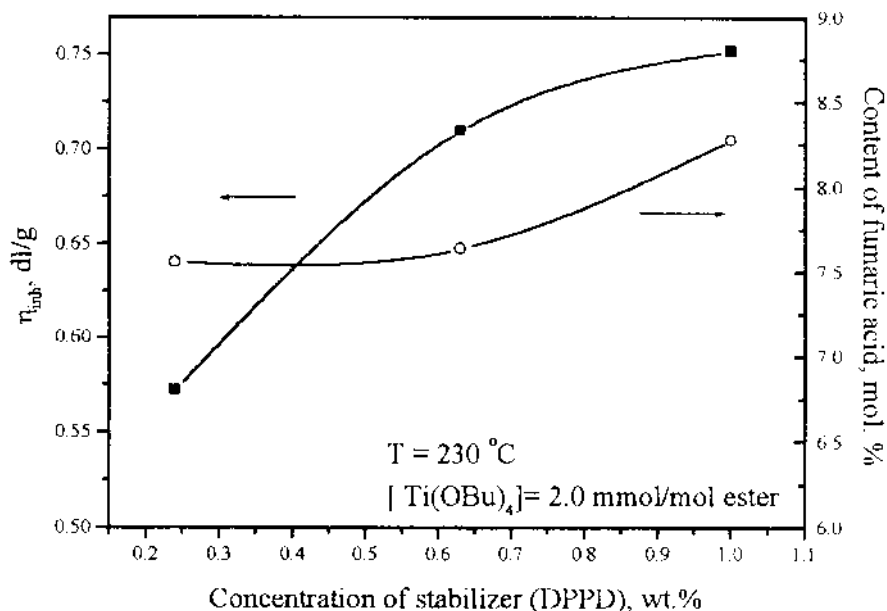


Fig. 2. Effect of thermal stabilizer (DPPD) concentration on the inherent viscosity and content of fumarate of the poly(ether-ester)s.

Copolyesters having inherent viscosities between 0.33 to 0.75 dl/g were obtained. The number average molecular weights of the poly(ester-ether)s in the series ranged from 5200 g/mol for TPE-4 to 7470 g/mol for TPE-7. It is obvious from Table I that the temperature of the second phase is very important and has a great influence on the molecular weights of the obtained poly(ester-ether)s.

It was also found that:

1) The concentration of catalyst has an important influence on the molecular weight of the obtained copolyester. For example, higher values of the inherent and complex dynamic viscosity were obtained when 2.0 mmol/mol ester was present than when the amount was 1.5 mmol/mol ester.

2) At temperatures above 230 °C the reaction rate increases and the viscosity of the reaction mixture increases so fast that it is very difficult to control the reaction and to stop it before crosslinking occurs. Thermal degradation becomes significant and limits the final degree of polymerization which can be attained. Also, the unsaturated double bonds are very sensitive to addition side reactions, leading to a variety of branched and crosslinked structures, at the higher temperature. Therefore it is necessary to add a thermal stabilizer before the polycondensation reaction to decrease thermal degradation and the occurrence of side reactions, *i.e.*, to protect the unsaturated double bonds.

3) The extent of the side reactions, *i.e.*, the decrease in the number of double bonds due to side reactions, can be controlled by the concentration of the thermal stabilizer and the polymerization temperature.

For the second stage of polycondensation, faster rates were observed at higher temperatures, as well as in the presence of fumaric acid derivatives. It may be concluded that the polycondensation temperature should not exceed 230 °C in order to prevent side reactions on the unsaturated double bonds of the fumaric acid moieties. If the polycondensation reaction is performed at 220 °C, a copolyester (TPE-8) with low molecular weight (lower than the critical molecular weight) was obtained even after a reaction time of 420 minutes.

It was found that a reaction time of 3 h at 230 °C under vacuum are the optimal conditions for these syntheses in the presence of 2.0 mmol/mol ester Ti(OBu)₄ and a DPPD concentration of 1 wt. %.

In a recent study it was also shown that the extent of double bond saturation in the

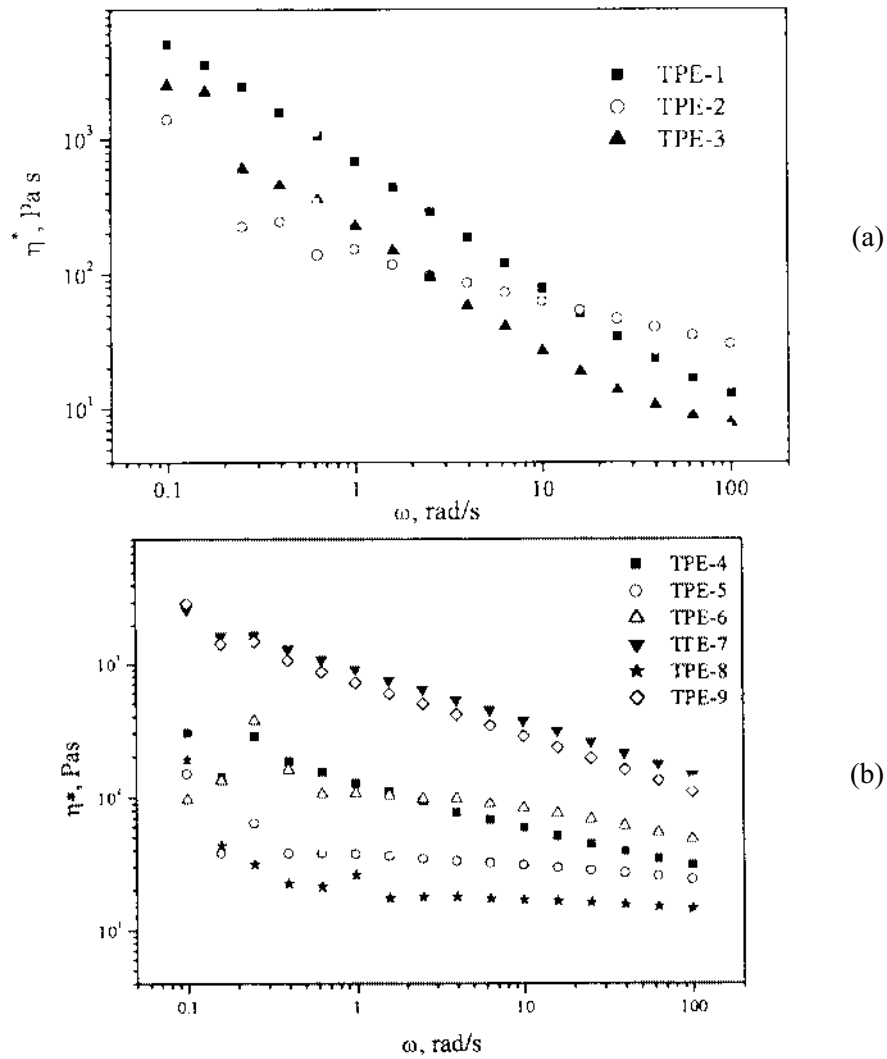


Fig. 3. Complex dynamic viscosity vs. frequency at 220 °C of the poly(ether-ester)s a) with insufficient thermostabilisation, b) with sufficient thermostabilization.

synthesis of fumarate-based polyesters increases with reaction temperature and diol concentration, as well as with the strength and concentration of the catalyst.¹⁶ The key to a successful synthesis of high molecular weight poly(ether-ester)s modified with an unsaturated acid is the combination of a highly effective catalyst and a thermal stabilizer, as well as the choice polymerization conditions which would protect the fumaric double bonds.

From the complex dynamic viscosity measurements it could be concluded that the thermostabilization was sufficient for the samples TPE 4-9 (Fig. 3.), because they show Newtonian and pseudoplastic behavior. While, in the melts of TPE 1-3, cross-linking occurred due to insufficient thermostabilization. The values of the complex dynamic viscosity η^* , shown in Tables I and II can be used as an indicator of the molecular weight of the samples. The relationship between the dynamic complex viscosity (η^*) at 220 °C and the inherent viscosity offer an idea about the overall length of the macrochain and indicates that values of η_{inh} around 0.7 dl/g correspond to the critical molecular weight above which macromolecular behavior exists (Fig. 4.).

Copoly(ether-ester)s with reasonably high molecular weights were obtained, as judged by the solution and melt viscosity measurements, as well as by ¹H-NMR analysis and by the ease with which fibers could be drawn from molten samples.

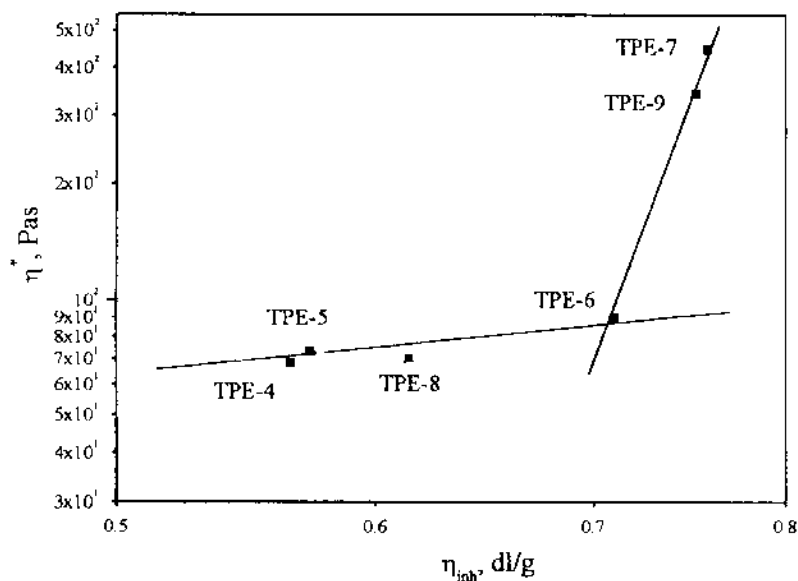


Fig. 4. Complex dynamic viscosity at 220 °C vs. inherent viscosity η_{inh} (points: experimental results; solid lines: linear regression) for poly(ether-ester)s modified with fumaric acid derivatives.

The number average molecular weights, \bar{M}_n , of the copoly(ether-ester)s were also deduced from the content of end groups, determined from ¹H-NMR measurements, with the assumption of a hydroxyl group at the end of a polymer chain. In the range of number average molecular weights from 5000 to 7500 g/mol, a linear dependency between \bar{M}_n and the inherent viscosity of uncrosslinked copolyesters exists (Fig. 5.). Two samples, TPE-1 and TPE-3, exhibit lower inherent viscosity than expected due

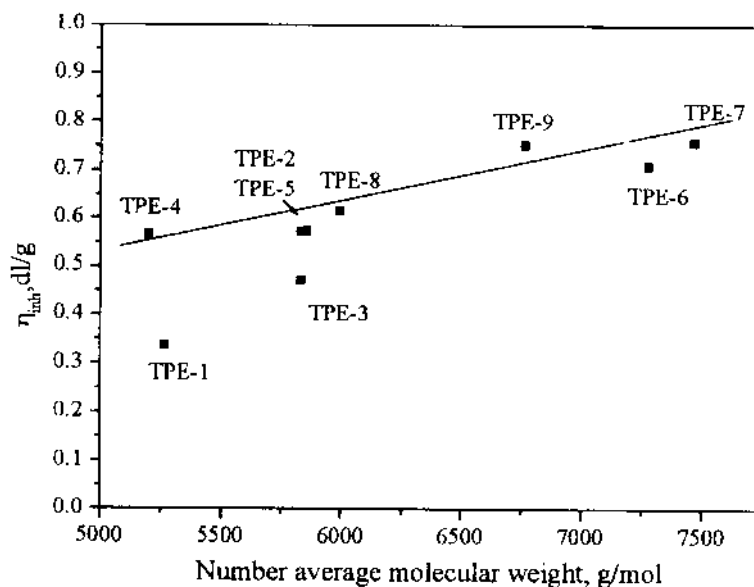


Fig. 5. Number average molecular weight (M_n) plotted against inherent viscosity for the uncrosslinked poly(ether-ester)s, (points: experimental results; solid lines: linear regression).

to their branched structure and smaller hydrodynamic volume, as can be seen from Fig. 5. The molecular weights of this series of poly(ether-ester)s modified with fumaric acid are lower compared to those of commercially available polymers in spite of their macromolecular behavior and good mechanical properties.

NMR analysis of the composition and structure

The molecular structure of the poly(ether-ester)s was confirmed by $^1\text{H-NMR}$ spectroscopy. The poly(ether-ester)s composition and molecular weight were determined from the $^1\text{H-NMR}$ spectra by integrating the corresponding proton resonance. The signal of the internal protons from the methylene groups in the residue of BD at the ends of the polymer chains $-(\text{CH}_2)_2-\text{CH}_2-\text{OH}$ appears at $\delta = 1.26$ ppm. The internal aliphatic protons from the residue of BD are in the region from 1.8 to 2.0 ppm, and the aliphatic protons from the polyether are in the region from 1.3 to 1.8 ppm. The signals of the aliphatic protons on the carbon atoms connected with oxygen $-\text{CH}_2-\text{O}-\text{CH}_2-$, in the residue of the polyether, appear at $\delta = 3.4$ ppm. A small triplet at 3.75 is due to $-\text{CH}_2-\text{OH}$ end groups. The signal of the protons from the methylene groups which are connected to esters groups, $-\text{OOC}-\text{CH}_2-$, appears at $\delta = 4.2-4.4$ ppm. The proton resonance at $\delta = 6.8$ ppm originates from the fumaric protons $-\text{CH}=\text{CH}-$, and the resonance at $\delta = 8.2$ ppm from aromatic protons. The peak of CHCl_3 appears at $\delta = 7.3$ ppm. The $^1\text{H-NMR}$ spectrum of the poly(ether-ester) TPE-4 is shown in Fig. 6.

The $^1\text{H-NMR}$ spectra confirmed that fumarate moieties are incorporated into the polymer chains, both in the hard and soft segments. The mol fraction of fumarate in the poly(ester-ether)s were calculated from the $^1\text{H-NMR}$ spectra using the equation:

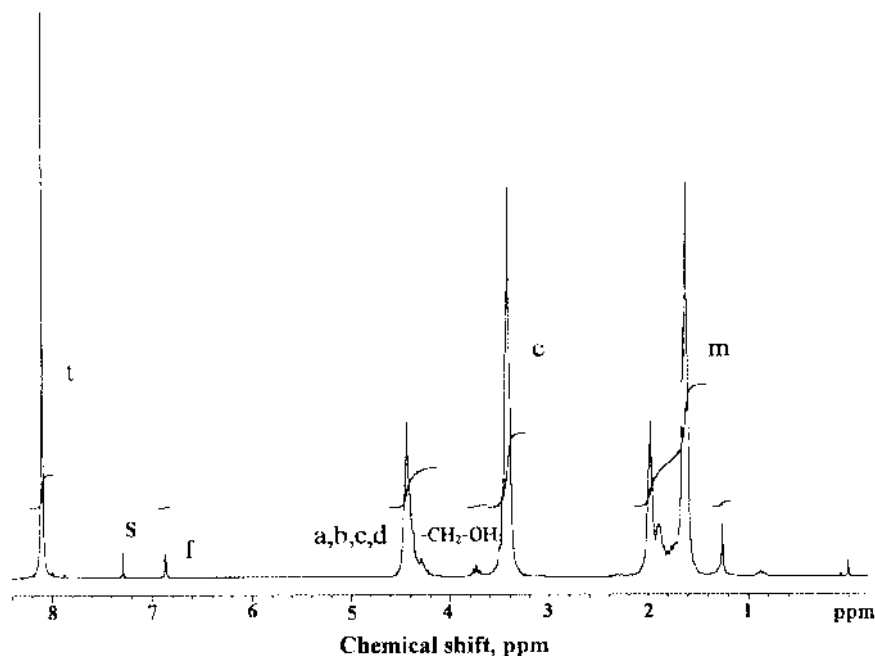


Fig. 6. $^1\text{H-NMR}$ spectrum of poly(ether-ester) TPE-4. For abbreviations see Fig. 7.

$$\text{Content of fumarate} = I(f)/2 / I(f)/2 + I(t)/4 \quad 100 \text{ mol } \%$$

where: $I(f)$ is the intensity of the signals of the fumaric protons and $I(t)$ the intensity of the signal of the aromatic protons.

The values calculated in this way agree with the values predetermined from the reaction mixture composition, see Table II.

The mole percents of the soft segments were calculated by the equation:

$$\text{Content of the soft segment} = I(e)/50.56 / I(t)/4 + I(f)/4 \quad 100 \text{ mol } \%,$$

where: $I(e)$ is the intensity of the signal from protons on carbon atoms connected with the oxygen in the polyethers, $\delta = 3.4$ ppm, and 50.56 the number of ether protons in the residue of the poly(tetramethylene oxide) ($\bar{M}_n = 1000$ g/mol).

The content of the hard segments was calculated simply by subtraction of the content of the soft segments from 100 mol %. These values are presented in Table II.

The mole ratio of the macrodiol/butenediol/terephthalate/fumarate in the product poly(ether-ester)s is also given in Table II. The found mole ratio is slightly different from the mole ratio in the starting reaction mixture (1:9.93:6.97:0.77).

The structure of the segmented thermoplastic poly(ether-ester)s based on terephthalic and fumaric esters is shown in Fig. 7, where: x —mole fraction of hard segments with terephthalate residues, y —mole fraction of hard segments with fumarate residues, z —mole fraction of soft segments with terephthalate residues, w —mole fraction of soft segments with fumarate residues.

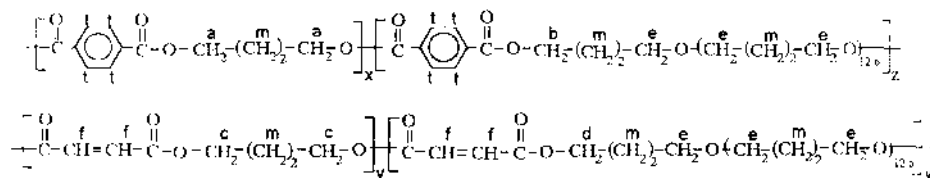


Fig. 7. Structure of the segmented thermoplastic poly(ether-ester)s based on terephthalic and fumaric acid derivatives.

TABLE II. Mole ratios and content of the hard and soft segments in poly(ether-ester)s from the $^1\text{H-NMR}$ spectra

Sample	Content fumarate mol%	BD	DMT	DMF	Hard segment on 1 mol PTMO	Hard segment mol %	Hard segment wt. %	inh dl/g	* Pa s
TPE-1	7.57	7.64	6.80	0.557	6.35	86.4	55.0	0.336	64.9
TPE-2	6.77	5.93	6.42	0.466	5.90	85.5	53.2	0.573	72.9
TPE-3	9.03	6.63	5.93	0.589	5.54	84.7	51.6	0.471	41.1
TPE-4	9.33	6.18	5.89	0.606	5.49	84.6	51.4	0.565	68.1
TPE-5	7.56	6.66	5.98	0.489	5.45	84.5	51.2	0.572	74.0
TPE-6	7.64	7.26	6.07	0.502	5.58	84.8	54.4	0.710	89.4
TPE-7	8.56	7.82	6.56	0.614	6.19	86.1	51.8	0.758	445.8
TPE-8	6.6	7.16	5.86	0.415	5.29	84.1	50.5	0.614	70.0
TPE-9	8.28	5.82	6.12	0.553	5.67	85.0	52.2	0.752	341.2

The total content of hard and soft segments were used for the calculation of the contents of fumarate and terephthalate in both the hard and soft segments with the assumption that these esters are proportionally incorporated into the segments.

The weight fraction of the hard segments in the polymers were in range from 50.5 wt. % (TPE-8) to 55.0 wt. % (TPE-1). It could be concluded that the terephthalate and fumarate residues were incorporated into the hard segments at the higher temperature rather than at the lower one. In all polymers the content of the hard segments was smaller than theoretical, but the variation was less than 5 %. From the values x , y , z and w , it can be concluded that both the terephthalate and fumarate react with BD rather than with PTMO, thus giving short segments.

The average lengths of the hard (PBT) segments were also calculated from the ratio of the peak intensities. These calculations are based on the assumption that the soft segment length is equal to the length of the starting polyether. The degree of polymerization of the PBT segments in the macrochain was between 5.29 and 6.35.

The average number of the repeating units, b , was calculated using the following equation:

$$I(-\text{CH}_2\text{OH}) / I(\text{t}) = 4 / [4 - n(\text{DMT}) - b]$$

The molecular weight of the repeating units, \bar{M}_{ru} , was calculated from the x, y, z, w values:

$$\bar{M}_{ru} = x \cdot 220 + y \cdot 170 + z \cdot 1130 + w \cdot 1082, \text{ g/mol}$$

The number average molecular weight of the polymer, \bar{M}_n , was calculated using the following equation: $\bar{M}_n = \bar{M}_{ru} \cdot b + 2 \cdot M(-O(CH_2)_4-OH)$, g/mol

$$M(-O(CH_2)_4-OH) = 178 \text{ g/mol}$$

The calculated values of b, \bar{M}_{ru} and \bar{M}_n are given in Table III.

TABLE III. The composition and average molecular weights of the poly(ether-ester)s determined from the $^1\text{H-NMR}$ spectra

Sample	Fumarate mol %	x	y	z	w	\bar{M}_{ru} g/mol	b	\bar{M}_n g/mol
TPE-1	7.57	5.875	0.481	0.925	0.0757	2507	2.03	5267
TPE-2	6.77	5.489	0.398	0.931	0.0676	2405	2.36	5854
TPE-3	9.03	5.023	0.499	0.907	0.090	2318	2.44	5834
TPE-4	9.33	4.983	0.513	0.907	0.093	2315	2.17	5200
TPE-5	7.56	5.053	0.413	0.927	0.076	2317	2.44	5831
TPE-6	7.64	5.147	0.426	0.923	0.076	2335	3.04	7278
TPE-7	8.56	5.648	0.529	0.912	0.085	2461	2.96	7470
TPE-8	6.6	4.928	0.349	0.932	0.066	2272	2.56	5994
TPE-9	8.28	5.202	0.470	0.918	0.083	2357	2.80	6764

The weight fraction of the hard segments in the polymers was calculated using the equation:

$$\text{Content of the hard segments} = (x \cdot 220 + y \cdot 170) / (\bar{M}_{ru}) \cdot 100 \text{ wt. \%}$$

Thermal properties of the copoly(ether-ester)s

The synthesized poly(ether-ester)s are partly crystalline and melting and glass transition temperatures were observed by DSC. Both the glass transition temperatures and the melting temperature vary slightly with composition (Table IV).

The crystalline fraction (w_c) was determined from the experimental heat of fusion (H_m) taking into account the corresponding expected weight fraction of PBT in the copolymer (H_{PBT}) using the equation:¹⁷

$$w_c = (H_m) / (w_h \cdot H_{PBT})$$

where: $H_{PBT} = 144.5 \text{ J/g}$, enthalpy of fusion of perfectly crystalline PBT and w_h weight fraction of the hard segments in the reaction mixture.

The crystalline fraction calculated from the DSC measurements and reduced to the corresponding weight fraction of PBT in the copolymer is slightly lower when

fumarate residues are present in the polymer. Modification with fumaric units also reduces the melting temperature of the poly(ether-ester)s.

The TGA curves of the copolyesters exhibit a 10 % weight loss ($T_{10\%}$) at 360 °C in the presence of nitrogen and 330 °C in the presence of oxygen. Residual weights of 7–8 % were registered in nitrogen. The thermal stability of the poly(ether-ester)s increased in an oxidative atmosphere when fumarate residues were present in the polymer chains.

TABLE IV. Thermal properties of the synthesized poly(ether-ester)s

Sample	Fumarate mol %	$T_m/^\circ\text{C}$	$H_m/\text{J/g}$	w_c	$T_g/^\circ\text{C}$	$T_{10\%}/^\circ\text{C}$ in nitrogen	$T_{10\%}^{\text{a)}}$ / $^\circ\text{C}$ in oxygen	$RW^{\text{b)}}$ 450/ $^\circ\text{C}$ in nitrogen
TPE-0	0	201	32.6	0.396	-70	361	330	7.4
PTE-10a ^{c)}	8.93	184	24.0	0.293	-64	363	346	8.2
TPE-10b ^{c)}	8.53	185	28.3	0.345	–	–	–	–

^{a)} $T_{10\%}$ is the temperature at which a 10 % weight loss was registered, heating rate 10 °C/min; ^{b)} Residual weight in nitrogen at 450 °C; ^{c)} Prepared under same reaction condition as the sample TPE-9.

CONCLUSION

The melt polycondensation of dimethyl esters of terephthalic acid with polyols and glycols, which has been successfully applied to the synthesis of poly(ether-ester)s, has been extended to include modification with dimethyl fumarate. The same two stage polymerization procedure involving transesterification and melt polycondensation could be employed for the introduction of unsaturated double bonds into the polyester chains. It was found that the optimal polymerization conditions are: a reaction time of 3 h at 230 °C under vacuum, in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ 2.0 mmol/mol acid and a DPPD concentration of 1 wt. %. The multiblock structure of the synthesized poly(ether-ester)s modified with fumaric acid derivatives was confirmed by NMR analysis. These thermoplastic copolyester elastomers, containing 10 mol % fumarate units in both the hard and soft segments exhibited lower melting temperatures and degree of crystallinity, compared to homopolyesters based on terephthalic acid, but showed higher elasticity and greater resistance towards oxidative degradation. The influence of the content of unsaturated bonds on the thermal and rheological properties of the poly(ether-ester)s will be discussed in a further publication.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИЗАЦИЈА ТЕРМОПЛАСТИЧНИХ ЕЛАСТОМЕРА МОДИФИКОВАНИХ ОСТАЦИМА ФУМАРАТА

ВЕСНА АЛЕКСАНДРОВИЋ И ЈАСНА ЂОНЛАГИЋ

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Серија поли(етер-естар)а на бази диметил терефталата (DMT), диметил фумарата (DMF), 1,4-бутандиола (BD) и поли(тетраметилен оксида) (PTMO, $M_n = 1000$ g/mol) је синтетисана двостепеним поступком који се састојао од трансестерификације и поликондензације у растопу. Молски однос полазних компоненти је тако одабран да

омогући константан масени однос (56:44) тврдих и меких сегмената у кополимеру. Садржај DMF је износио 10 mol %, рачунато на укупну количину унетих естара. Синтеза ових термопластичних еластомера је оптимизована у погледу концентрације катализатора тетра-*n*-бутил-титаната, Ti(OBu)₄, и стабилизатора *N,N'*-дифенил-*p*-фенилендиаминa, DPPD, као и у погледу температуре. Састав и структура синтетисаних поли(етар-естар)а су одређени из ¹H-NMR спектра. Моларна маса средња по бројној заступљености синтетисаних полимера, израчуната из NMR спектра, упоређена је са одговарајућим вредностима инхерентних вискозитета, одређених у крезолу, и комплексних динамичких вискозитета (η^*) растопа. Утицај садржаја фумарата на термичка својства синтетисаних кополиестара је изучаван диференцијалном динамичком калориметријом (DSC) и термичком гравиметријском анализом (TGA).

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