

Copolymers of Glycerol and Propylene Glycol Diglycidyl Ethers with Aromatic Dithiols

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ABSTRACT: Monomers derived from renewable resources have the potential to become the biobased alternatives for petroleum derived chemicals in the production of polymers. Glycerol, the byproduct of biodiesel refining, and propylene glycol derived from glycerol are promising candidates which can be used in the synthesis of polymers as they are or after chemical modification. The new copolymers of glycerol and propylene glycol diglycidyl ethers with aromatic dithiols were synthesized and investigated in this study. Their chemical structures were confirmed by IR, ¹H-NMR spectroscopy, and gel permeation chromatography. The dependencies of the mechanical, thermal properties, swelling in the different solvents, biodegradability, and bioresistance of synthesized copolymers on their chemical structures were studied. The properties of some synthesized copolymer films were found to be comparable with those of commodity polymer films. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 4367–4374, 2013

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INTRODUCTION

The recent development of polymeric materials derived from renewable raw materials attracts the attention of both scientists and manufacturers due to the continuous rise of consumer needs for plastics and rapidly depleting oil reserves. In addition, the use of materials derived from renewable raw materials enables production of both stable and biodegradable polymers for long-term or short-term use, respectively. Such products often exhibit properties similar to those of conventional polymers, i.e. petroleum-derived, and decompose into harmless substances after use and release into the environment.

Biodiesel is a fuel composed of monoalkyl esters of long-chain fatty acids derived from renewable vegetable oils or animal fats. The predominant biodiesel production process involves a phase of transesterification that yields glycerol as a by-product.¹ Recent increases in glycerol production from biodiesel refining has provided a good opportunity to find new applications for glycerol as it is or after chemical modification for a very wide spectrum of different uses in the sectors of energy, feed preparation, technical aids, and fine chemistry.^{2–5} Glycerol has the potential to become an important feedstock chemical used for

the production of new chemical products as well as biobased alternatives for many petroleum derived chemicals.^{6–8} A recent significant advance is the development of a synthetic route to propylene glycol (1,2-propanediol) from glycerol, which represents a viable alternative to the classic petrochemical route from propylene.^{9–12} Both glycerol and propylene glycol directly or after chemical modification can be used as monomers in the synthesis of polymers.

In this study, the diglycidyl ethers of glycerol and propylene glycol were chosen as monomers for the synthesis and investigation of new copolymers due to the many excellent features of epoxy groups. Epoxides are important synthetic intermediates widely employed in the synthesis of thermosetting polymers which are extensively used in adhesives, paints, coatings, medical implants, and electrical devices because of their high specific strength and stiffness, good thermal stability, excellent adhesion properties, electrical insulating properties, corrosion resistance, chemical compatibility with reinforcing fibers, and relative ease-of-manufacture.^{13–18} Dithiols were chosen as comonomers in this study due to their high reactivity with the epoxy groups, even at ambient or sub-ambient temperatures.^{19–24}

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The aim of this work was not only to synthesize new copolymers and investigate their properties but also to show the possibility of use of the monomers derived from renewable resource for the synthesis of polymers with the properties comparable with those of conventional polymers.

EXPERIMENTAL

Materials

Glycerol diglycidyl ether (technical grade, Aldrich), propylene glycol diglycidyl ether (99%, Chemos), 4,4'-thiobisbenzenthiole (98%, Aldrich), benzen-1,3-dithiol (99%, Aldrich), biphenyl-4,4'-dithiol (95%, Aldrich), and triethylamine (99.5%, Aldrich) were used as received. Tetrahydrofuran (99%, Eurochemicals), *N,N*-dimethylformamide (99%, Lachema), chloroform (99%, Lach-Ner), and toluene (Delta-Chem) were purified and dried by the standard methods.²⁵

Instrumentation

¹H-NMR spectra were recorded with Varian Unity Inova spectrometer at 300 MHz using CDCl₃ as a solvent. All the data are given as chemical shifts δ (ppm) downfield from (CH₃)₄Si. FTIR spectra were recorded on a Perkin Elmer Spectrum BX II FTIR spectrometer. The spectra of the solid materials were recorded using KBr pellets.

The average molecular weight and the molecular weight distribution were estimated by gel permeation chromatography (GPC) using Waters SEC system including a Waters Lambda-Max Model 481 LC spectrophotometer, Viscotek column G2500H_{HR} and GMH_{HR}-M system, and polystyrene standards.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Universal V4.1D TA Instruments apparatus at a 10°C min⁻¹ heating rate under nitrogen atmosphere.

Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PC Luxx apparatus in the temperature range from the room temperature to 650°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere (nitrogen flow rate 100 mL min⁻¹).

The swelling value of the films of the synthesized copolymers was obtained by measuring the volume of samples swollen in distilled water, chloroform, and toluene.

The glassy container comprised of two spherical parts of 50 mL joined by a tube graduated with the accuracy of 0.1 mL was used. One spherical part was separated from the graduated tube by a liquid permeable partition. This spherical part was fitted with the neck closed by stopper. The swelling agent was poured and the sample was placed in through this neck. The initial volume of the copolymer film was measured before placing into the measuring container. The measuring container was kept in such position that a sample was immersed in the swelling agent during the test and turned in such position that the liquid leaked to another side of the container at the certain intervals of time. The change of the volume of the swelling agent was measured. The swelling value was calculated by the following equation:

$$\alpha = \frac{V - V_0}{V_0} \times 100 \quad (1)$$

where α is the swelling value, (%); V_0 is the initial volume of the sample, (mL); V is the volume of the swollen sample, (mL).

The volume of the swollen sample was estimated by the following equation:

$$V = V_0 + V_a \quad (2)$$

where V_a is the volume of the absorbed swelling agent, (mL).

The arithmetic average of the swelling values of three film samples (20.00 (± 0.00) mm \times 20.00 (± 0.00) mm \times 0.05 (± 0.01) mm) of each copolymer was calculated. The variation of experimental results did not exceed 5% within the group.

The stress-strain curves of the films were obtained with a material testing machine BDO-FB0.5TH (Zwick/Roell). The strain rate for tensile test of all the samples was 1 mm min⁻¹. The width of the films was 5.00 (± 0.00) mm, the thickness of the films was 0.05 (± 0.01) mm. The arithmetic average of the results of the three-six film samples of each composition was calculated. Only the results, the variation of which did not exceed 15% within the group, were taken for the calculation of the arithmetic average.

The hardness of the films was estimated with a Hepler consistency meter by pressing a steel cone with an angle of 53°08' into the specimen under a load of 1500 g for 60 s. The arithmetic average of the hardness of three film samples (thickness 0.05 (± 0.01) mm) of each composition was taken. The variation of experimental results did not exceed 5% within the group. The hardness of the films was calculated using eq. (3):

$$H_H = \frac{F}{S} = \frac{4 \cdot F}{\pi \cdot \Delta h^2} \quad (3)$$

where H_H is the hardness of a specimen (Newton mm⁻²), F the force acting on the specimen (Newton), S is the surface area of the circular patch of the specimen that interacts with the cone, Δh is the depth of penetration of the cone into the specimen (mm).

Synthesis of Copolymers

A stoichiometric ratio of 1 : 1 {diglycidyl ether (glycerol diglycidyl ether or propylene glycol diglycidyl ether)} and {dithiol (4,4'-thiobisbenzenthiole, benzen-1,3-dithiol, or biphenyl-4,4'-dithiol)} was used in the synthesis of copolymers. Triethylamine (10 mol % from amount of diglycidyl ether) was used as catalyst. Diglycidyl ether was mixed with dithiol dissolved in minimal amount (~ 0.5 mL) of tetrahydrofuran. Then triethylamine was added. The reaction mixture was stirred rigorously with a magnetic stirrer, poured on a plastic film, and kept at 50°C for 2–3 h until the hard film was obtained.

Copolymers **1–6** IR (KBr): $\nu = 3386\text{--}3424$ (O—H), 3068–3000 (Ar. C—H), 2968–2865 (Alk. C—H), 1593–1570, 1475–1463 (Ar. C=C), 1140–1092 (C—O—C), 1097–1087 (Alk. C—S), 937–935 (Ar. C—H) cm⁻¹ (see Supporting Information Figure S1).

Copolymer **6** and soluble in chloroform fractions of copolymers **4** and **5** ¹H-NMR (300 MHz, CDCl₃, δ): 1.15 (s, CH₃), 1.78 (s, OH), 2.96–3.18 (m, O—CH₂), 3.40–4.02 (m, O—CH₂),

$\text{CH}_3\text{—CH}_2\text{—S—CH}_2$), 7.05–7.51 (m, Ar) (see Supporting Information Figure S2).

Soxhlet Extraction

The samples of the bulk polymers (0.2 g) were extracted with chloroform for 24 h using a Soxhlet extractor. After the extraction, the solvent was evaporated to obtain the soluble part of the bulk polymer. The soluble and insoluble fractions were dried under vacuum until no changes of the weight were observed.

Biodegradability by Soil Burial Test

The 5 L volume chambers filled with soil from organic farming (sandy loam Haplic Luvisol; pH_{KCl} , 5.8; humus, 1.284%; the moisture content (20–30%)) were used for the copolymer biodegradability tests. The copolymer specimens (10.00 (± 0.00) mm \times 10.00 (± 0.00) mm) were put into 50.00 (± 0.00) mm \times 60.00 (± 0.00) mm polychlorvinyl bags with 0.05 mm mesh diameter, buried into the soil, and incubated at (26 \pm 2) $^\circ\text{C}$. After three months the specimens were removed and analyzed regarding the fungal colonization and their weight loss. For isolation of degrading fungi, the specimens were removed from the soil, washed with sterile physiological water (0.9% NaCl in distilled water), and their replicas were made on Malt Extract Agar with chloramphenicol (50 mg L $^{-1}$) to stop bacterium growth. Isolated fungi were purified and identified according to the morphological features. The biodegradability of the copolymers was estimated according to their relative weight loss: $(a - b)/a \times 100\%$, where: a is the initial weight of the specimen (g); b is the specimen weight after incubation. The copolymer specimens were weighed by means of an analytical balance with high precision (± 0.001). For the soil microbial activity estimation the cotton wool (1 g) was buried.

Bioresistance by Environmental Chamber Method

The selected copolymer specimens were rinsed with sterile distilled water, blotted dry, and inoculated with fungal suspension of 10^6 spores mL $^{-1}$ concentration (10 μL in 1 cm 2). The fungal strains (*Aureobasidium pullulans* (de Bary) G. Arnaud15-03, *Eurotium chevalieri* L. Mangin (= *A. chevalieri* L. Margin) 0502-06, and *Eurotium herbariorum* (Wiggers: Fr.) Link (= *Aspergillus glaucus* (L.) Link) 0459-05 used were taken from the collection of the Biodeterioration Research Laboratory of the Nature Research Centre (Lithuania). They were selected as fenoloxidase, lipase, amylase, pectinase, and endogluconase producers. The inoculated specimens were placed into the chamber (>90% relative humidity) and incubated at (26 \pm 2) $^\circ\text{C}$ for three months. The control specimens were not inoculated with the fungal suspension. Monthly visual assessment of the degree of specimen colonization was performed using four-grade scale²⁶:

- Grade 0—no growth apparent even under the microscope;
- Grade 1—growth invisible or hardly visible to the naked eye but clearly visible under microscope;
- Grade 2—slight growth covering less than 25% of the specimen surface;
- Grade 3—growth covering more than 25% of the specimen surface.

The bioresistance of the copolymers was estimated according to the percentage of their weight change after 3 months as described above.

RESULTS AND DISCUSSION

Synthesis of Copolymers

The possible structures of copolymers 1–3 synthesized by the reaction of glycerol diglycidyl ether and three different dithiols (4,4'-thiobisbenzenthioi, benzen-1,3-dithioi, and biphenyl-4,4'-dithioi) are presented in Figure 1.

The possible structures of copolymers 4–6 synthesized in the reaction of propylene glycol diglycidyl ether and 4,4'-thiobisbenzenthioi, benzen-1,3-dithioi, and biphenyl-4,4'-dithioi are presented in Figure 2.

S—H groups of dithiols react very readily with the epoxy groups of diglycidyl ethers. This leads to the easy formation of macromolecules. Moreover, epoxy groups can react with hydroxy group of glycerol diglycidyl ether and hydroxy groups formed newly after the ring-opening of epoxy groups. This leads to the formation of the branched or even crosslinked structures beside linear macromolecules what confirmed the insoluble fractions of copolymers obtained after Soxhlet extraction of copolymers 1–5 in chloroform.

Copolymer 6 is soluble in common organic solvents such as acetone, chloroform, and tetrahydrofuran at room temperature. Copolymers 1–5 swell in common organic solvents. The yields of insoluble fraction of copolymers 1–5 obtained after Soxhlet extraction in chloroform are presented in Table I. The significantly higher yield of insoluble fraction was established for glycerol diglycidyl ether copolymers 1–3 in comparison with propylene glycol diglycidyl ether copolymers 4 and 5. The formation of more crosslinked structures than linear or branched structures during the reaction of glycerol diglycidyl ether with dithiols was predetermined by higher amount of functional groups that can participate in the formation of the crosslinks.

The structure of copolymers was confirmed by IR, $^1\text{H-NMR}$ spectrometries. The molecular weights of the soluble copolymers were estimated by GPC. The signals of epoxy groups at 910 cm $^{-1}$ and 801 cm $^{-1}$ which are present in the IR spectra of diglycidyl ethers, as well as signals of S—H group absorption at 2556 cm $^{-1}$ which are present in the IR spectra of dithiols, disappeared in the IR spectra of all copolymers 1–6. The characteristic C—S stretch at 1097–1087 cm $^{-1}$ appeared in the IR spectra of copolymers 1–6. The significant increase of the intensity of O—H stretch at 3386–3424 cm $^{-1}$ in the IR spectra of copolymers 1–6 shows the formation of hydroxy groups. Both, the hydroxy groups of glycerol diglycidyl ether and hydroxy groups formed newly after the ring-opening of epoxy groups of diglycidyl ethers, can participate in the formation of the crosslinks in the copolymers 1–6. For the illustration of the above stated, the IR spectra of propylenglycol diglycidyl ether, 4,4'-thiobisbenzenthioi, and copolymer 4 are presented in Supporting Information Figure S1.

The signals in the $^1\text{H-NMR}$ spectra of copolymer 6 and soluble in chloroform fraction of copolymers 4 and 5 can be assigned

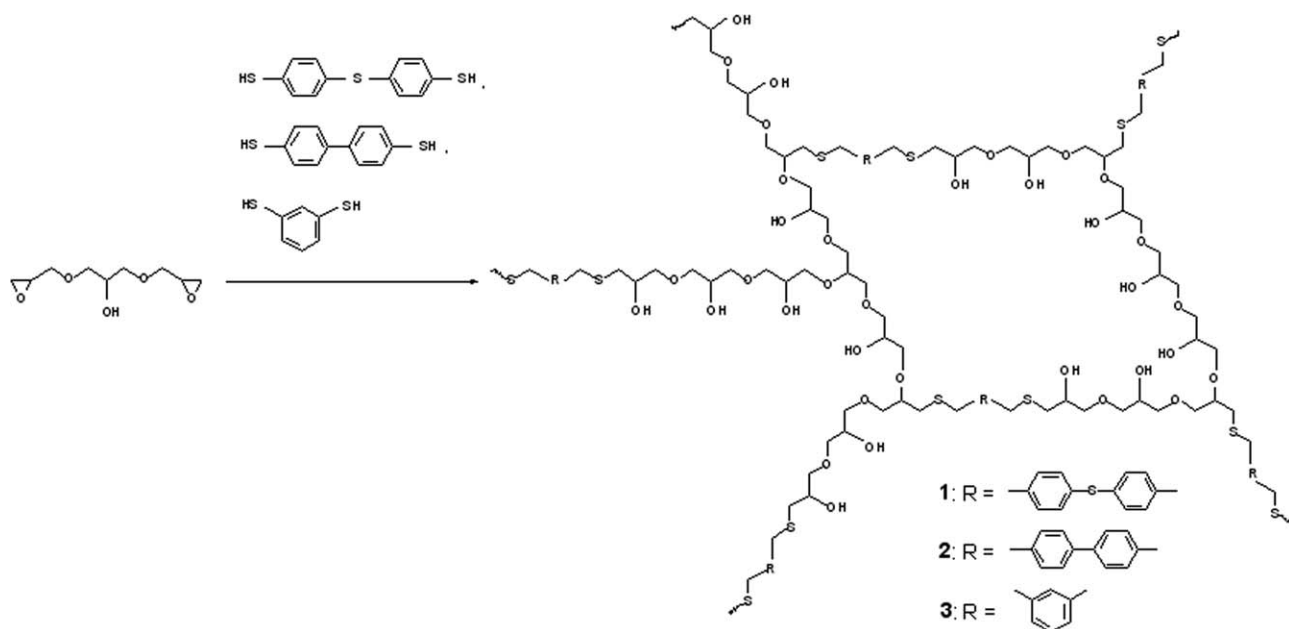


Figure 1. Synthesis of glycerol diglycidyl ether copolymers 1–3.

to the characteristic hydrogen atoms of these compounds. The proton signals of S—H group at 3.48–3.53 ppm which are present in the spectra of dithiols, as well as the proton signals of epoxy groups at 2.57 and 2.76 ppm which are present in the spectra of propylene glycol diglycidyl ether disappear in the spectra of copolymers 4–6. As an example, the $^1\text{H-NMR}$ spectra of benzen-1,3-dithiol, propylenglycol diglycidyl ether, and copolymer 6 are presented in Supporting Information Figure S2.

Thermal Properties

DSC confirmed that synthesized copolymers 1–6 are amorphous materials. Only a glass transition was observed in the DSC curves of all copolymers. As an example, the DSC thermograms of copolymer 6 are presented in Supporting Information Figure S3. The glass transition temperature (T_g) of copolymers 1–6 is in the range from 33°C to 59°C (Table I).

Copolymers 1–6 exhibit relatively high thermal stability as was determined by TGA. Their thermal degradation temperatures at

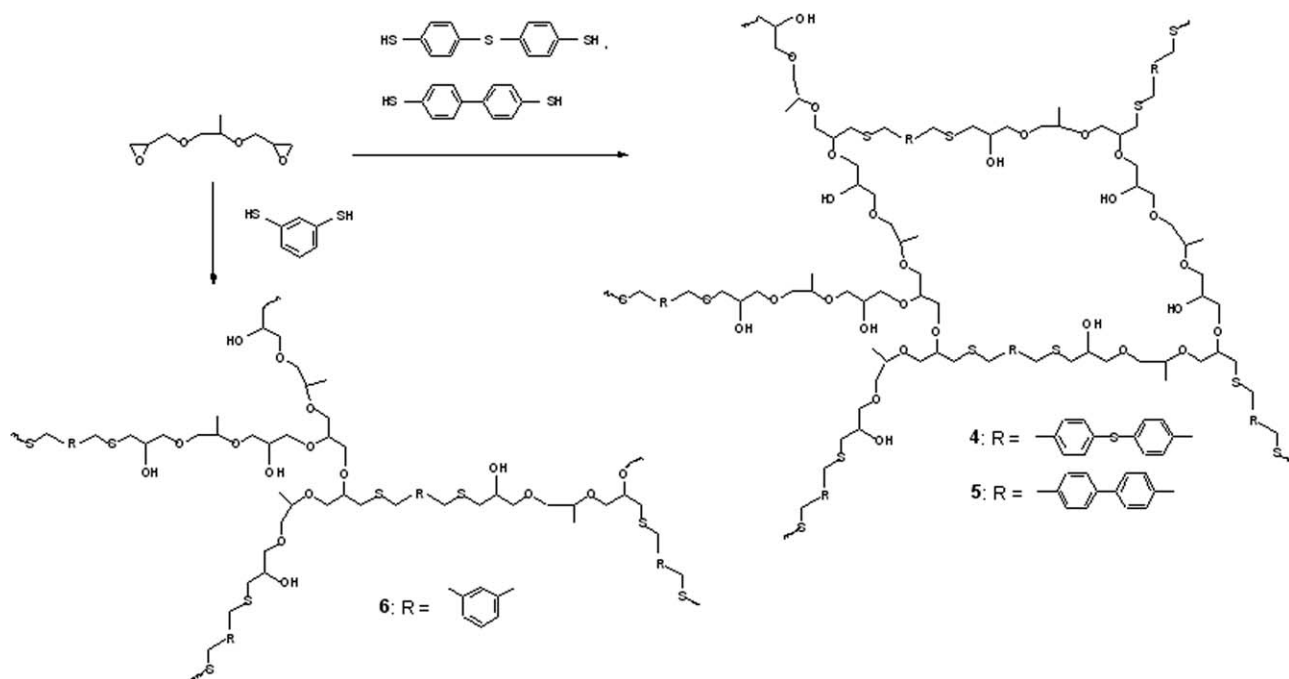


Figure 2. Synthesis of propylene glycol diglycidyl ether copolymers 4–6.

Table I. The Selected Characteristics of Copolymers 1–6

Copolymer	Insoluble fraction in chloroform (%)	M_n	M_w	M_w/M_n	T_g^b (°C)	$T_{deg.-10\%}^c$ (°C)
1	90	–	–	–	33	290
2	92	–	–	–	45	245
3	80	–	–	–	58	260
4	40	1230 ^a	10,070 ^a	8.2 ^a	53	264
5	43	2570 ^a	13,910 ^a	5.4 ^a	55	273
6	0	1350	3360	2.6	59	230

^a Average molecular weights and polydispersity of copolymer fraction soluble in tetrahydrofuran.

^b Glass transition temperature.

^c Degradation temperature at the weight loss of 10%.

the weight loss of 10% are in the range of (230–290)°C (Table I). The soluble copolymer 6 showed the lowest 10% weight loss temperature.

Swelling

The swelling of copolymer films in polar and non-polar solvents is important in terms of their potential application. In addition, investigation of swelling behavior gives some information on the structure–properties relationship of polymers. The dependency of the swelling value on the swelling time of copolymers 1–5 was estimated in distilled water (Figure 3), non-polar organic solvent toluene (Figure 4), and polar organic solvent chloroform (Figure 5) at room temperature.

The highest swelling values of copolymers 1–4 was observed in distilled water (Figure 3). This observation can be explained by the hydrophilicity of the copolymers. The highest swelling rate in all the solvents used was observed for copolymer 3 due to its more flexible macromolecular chains with less aromatic fragments as compared to the other copolymers. The degree of swelling of copolymer 3 in distilled water reached 1300%. In toluene and chloroform it reached 400%. Copolymer 3 reached the maximum degree of swelling in distilled water after 30 min, while other copolymers only after 50 min (Figure 3). The similar behavior was observed in toluene. Copolymer 3 reached the

highest degree of swelling in toluene after 20 min while the other copolymers only after 30–40 min (Figure 4). In chloroform, copolymer 3 reached the maximum degree of swelling after 30 min, copolymers 2 and 4 after 40 min. Copolymer 1 reached the maximum swelling degree in chloroform after 10 min, and it was the lowest maximum swelling degree among all the studied copolymers (Figure 5).

The consistent pattern of showing the higher swelling values in distilled water than in organic solvents is not valid for copolymer 5. The film of copolymer 5 attained the highest degree of swelling in chloroform (400%). In toluene this value was 300%, and only 100% in distilled water. This observation can be explained by the higher hydrophobicity of copolymer 5.

Mechanical Properties

The hardness values of the films of copolymers 1–5 measured by Hepler consistometer are summarized in Table II. The glycerol diglycidyl ether based copolymers 1 and 2 showed the higher hardness values than the corresponding propylene glycol diglycidyl ether based copolymers 4 and 5. The observed hardness values of the films of copolymers 1, 2, 4, and 5 having higher share of aromatic fragments in main chains were higher than that of the film of copolymer 3 having less aromatic fragments. The hardness of the films of copolymers 2, 4, and 5 vary from 850 N mm⁻² to 900 N mm⁻² and were found to be

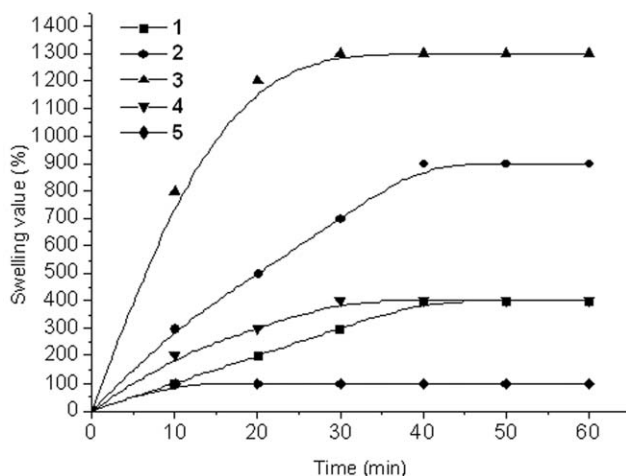


Figure 3. The swelling kinetic curves of the copolymers 1–5 in distilled water.

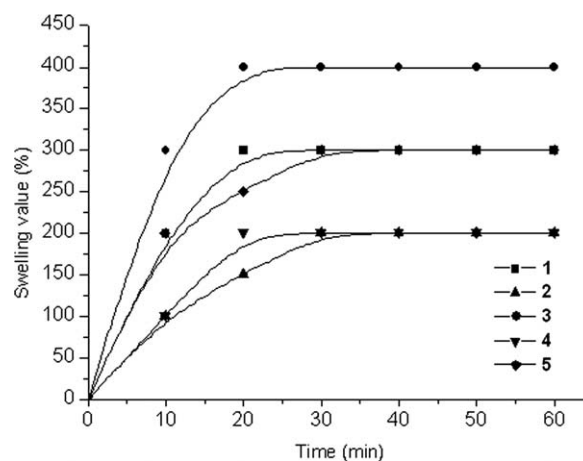


Figure 4. The swelling kinetic curves of the copolymers 1–5 in toluene.

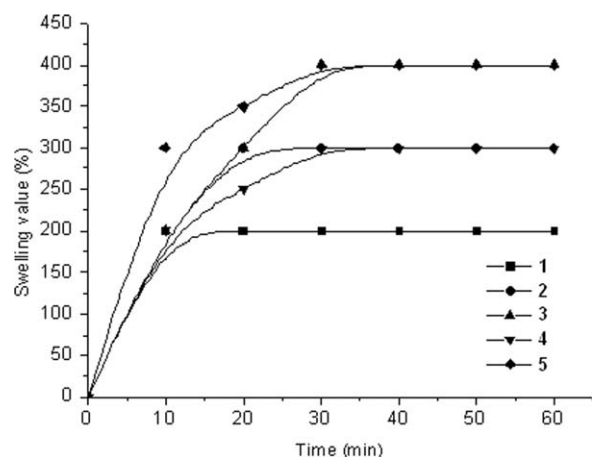


Figure 5. The swelling kinetic curves of the copolymers 1–5 in chloroform.

higher than those observed for the commodity polymer films such as low density polyethylene (PE_LD), polypropylene (PP), and polyvinylchloride (PVC) ((250–550) N mm⁻²) established at the same experimental conditions. The hardness of the film of copolymer 1 is similar to that of polyethylene terephthalate (PET) film (690 N mm⁻²) established at the same experimental conditions. The hardness of the film of copolymer 3 is similar to that of PE_LD film (460 N mm⁻²) established at the same experimental conditions.

The mechanical characteristics of the films of copolymers 1–5 estimated by the stress–strain tests are summarized in Table II. The dependence of the mechanical properties on the chemical structure of copolymers was observed. The highest tensile strength exceeding 19 MPa was demonstrated by the films of copolymers 2 and 5 having rigid biphenyl-4,4'-dithiol fragments in the main chains. The lowest tensile strength was demonstrated by the film of copolymer 3 having benzen-1,3-dithiol fragments. The tensile strength of the films of all copolymers (1–5) was lower than that of the commercial polymer films established at the same experimental conditions ((26.37–68.31) MPa for PE-LD, PP, PVC, and 190.08 MPa for PET).

The highest elongation at break was demonstrated by the films of copolymers 1 and 4 having 4,4'-thiobisbenzenthiole fragments in their backbones. The elongation at break of copolymer 1 is comparable with that of the PET (12.63%) and PP (24.20%) films established at the same experimental conditions. The elongation at break of the other synthesized copolymers was significantly lower.

The films of copolymers 1–5 can be regarded as soft materials according to the established Young modulus values. The highest Young modulus was demonstrated by copolymer 5 with biphenyl-4,4'-dithiol fragments in the main chain. It was even higher than that of PP (20.94 MPa) and PE-LD (27.18 MPa) established at the same experimental conditions. The Young modulus values of the other synthesized copolymers were lower than those of the commercial polymer films established at the same experimental conditions.

Biodegradability and Bioresistance

Biodegradation is a relatively rapid process under appropriate conditions of moisture, temperature, and oxygen availability.²⁶

The biodegradability of the copolymers was tested using soil burial experiment in the laboratory under the temperature and humidity optimal for fungi development. After three months exposure in the soil all tested copolymers showed the mass loss which differed depending on their chemical structure (Figure 6). The highest value of the weight loss of 20.49% was recorded for the sample of glycerol diglycidyl ether based copolymer 3 with the lowest content of aromatic species in the main chain, however it was 1.4 times lower than that of the cotton wool (cellulose). The lowest mass loss of 4.24% was observed for the sample of copolymer 4. Visually no any conspicuous alterations of specimens were observed. Only some surface swellings were noticed and the specimens were a little softer, apparently because of the soil humidity.

Soil is rich in various microorganisms with different enzymatic activity. They can use materials of different chemical composition as nutrient substrata and consequently decompose them. The present soil burial test showed that there was some fungal species able to develop on the copolymer specimens tested and that they could be degraded to some degree by soil inhabiting fungi. During three month fungi of five different genera were isolated from the buried copolymer specimens (Table III). *Gliocladium catenulatum* was detected on all tested specimens and *Fusarium sp.* was detected on all tested specimens except that of copolymer 3.

There are reports that poly(3-hydroxybutyrate), (poly(3-hydroxybutyrate)), and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) were degraded in soil by fungi mainly from *Aspergillus* and *Penicillium* genera^{27,28} and it was revealed that *Aspergillus niger* was capable of degrading even polyethylene.²⁹ In the present experiment, *Aspergillus sp.* that was detected on cotton wool was observed on the copolymer specimens only in early exposition stage (after 1 month) but later it likely was concurred by *G. catenulatum* and *Fusarium sp.* that are considered as strong antagonists. *A. niger* was isolated from the samples of copolymers 4 and 6 after three months of exposition.

The estimation of the bioresistance of copolymers by environmental chamber method confirmed that the specimens tested

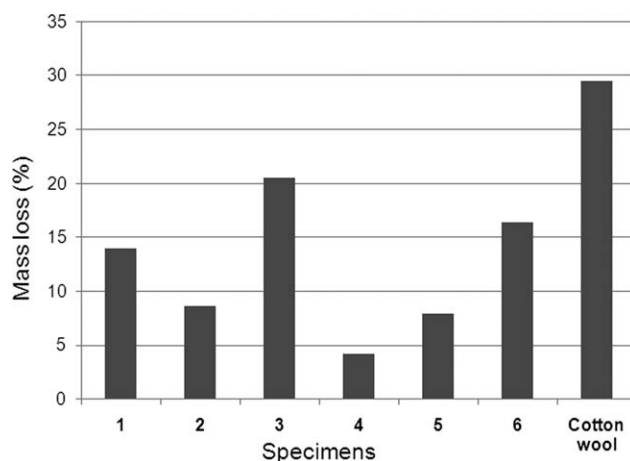


Figure 6. Mass loss of the samples of copolymers 1–6 after 3 months exposition in soil.

Table II. Mechanical Characteristics of Copolymer 1–5 Films

Copolymer	Hardness, (N mm ⁻²)	Tensile strength (MPa)	Elongation at break (%)	Young modulus (MPa)
1	690	5.28	18.21	16.22
2	870	19.23	0.59	31.00
3	440	4.44	0.22	3.48
4	900	8.32	8.31	14.00
5	850	19.41	6.95	55.80

Table III. Fungi Isolated from the Samples of Copolymers 1–6 and Cotton Wool After Exposition in Soil

Fungi	Copolymers						Cotton wool
	1	2	3	4	5	6	
<i>Aspergillus niger</i>				+		+	
<i>Aspergillus sp.</i>							+
<i>Fusarium sp.</i>	+	+		+	+	+	
<i>Gliocladium catenulatum</i>	+	+	+	+	+	+	
<i>Stachybotrys sp.</i>							+
<i>Zygorhynchus moelleri</i>	+						
<i>Mycelia sterilia</i>		+					

could be damaged by fungi (Table IV). The development of *A. pullulans* 15-03 was noticed on the tested specimens already after 1-month incubation and it reached two grades according to the four-grade scale. The fungal growth was restricted to the inoculation point. However, the growth of *E. chevalieri* 0502-06 and *E. herbariorum* 0459-05 was hardly visible. In the course of incubation the fungal colonization increased on all the samples except *A. pullulans* 15-03 growth on the sample of copolymer 3 and the sample of copolymer 4, and *E. chevalieri* 0502-06 on the sample of copolymer 1. It could be supposed that in the latter cases fungi have limited potential to assimilate polymers of this chemical composition as nutrient source and consequently their growth stopped. After 3 months the greatest fungal colonization was recorded on the sample of copolymer 1 by *A. pullulans* 15-03 and *E. herbariorum* 0459-05, and on the sample of

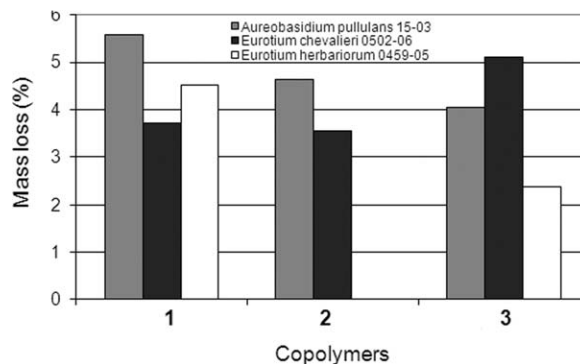


Figure 7. Mass loss of the samples of copolymers 1, 3, and 4 due to the fungal colonization after 3 months

copolymer 4 by *E. chevalieri* 0502-06. It reached more than 25% of the specimen surface but the colonies were sparse.

The results showed that the copolymers tested were not resistant to fungal attack and contained available nutritive substance for them though the resistance of copolymers depended on the fungus species attacking it and their chemical composition.

During the environmental chamber experiment the highest mass loss of 5.59% caused by *A. pullulans* 15-03 was observed for the sample of copolymer 1. This result correlates with visual evaluation of the fungal growth on the surface (Figure 7). The lowest mass loss of 2.38% was caused by *E. herbariorum* 0459-05 colonizing the sample of copolymer 4.

Table IV. Colonization by Fungi on the Samples of Selected Copolymers in Environmental Chamber (Evaluation According Four-Grade Scale)

Copolymer	Fungus	Incubation period		
		1 month	2 month	3 month
1	<i>Aureobasidium pullulans</i> 15-03	2	3	3
	<i>Eurotium chevalieri</i> 0502-06	1	2	2
	<i>Eurotium herbariorum</i> 0459-05	1	2	3
3	<i>Aureobasidium pullulans</i> 15-03	2	2	2
	<i>Eurotium chevalieri</i> 0502-06	1	1	1
4	<i>Aureobasidium pullulans</i> 15-03	2	2	2
	<i>Eurotium chevalieri</i> 0502-06	1	2	3
	<i>Eurotium herbariorum</i> 0459-05	1	1	2

Comparison of the results obtained two methods shows that the higher mass loss of copolymers was observed after their exposition in the soil where the whole complex of fungi with various enzymatic activities attacked them. During the soil burial test the mass of copolymer 1 decreased 2.5 times more than after its inoculation with a single *A. pullulans* 15-03 culture.

The results of the studies of bioresistance showed that all the synthesized copolymers may be biodegradable under favorable conditions for fungi growth; however the extent of biodegradation depended on the structure of copolymers and on fungal species.

CONCLUSIONS

The copolymers were prepared by polyaddition reactions of glycerol and propylene glycol diglycidyl ethers with various aromatic dithiols. They were found to be amorphous materials with the glass transition temperature in the range from 33°C to 59°C. Their thermal degradation temperatures at the weight loss of 10% are in the range of (230–290)°C. The dependencies of the mechanical and swelling properties of the copolymers on their chemical structures were studied. The highest degrees of swelling of for the studied copolymers were observed in water which reached 1300%. The degrees of swelling in toluene and chloroform reached 400%. The hardness of the polymer films ranged from 443 N mm⁻² to 900 N mm⁻². The Young modulus ranged from 0.53 MPa to 55.80 MPa. The mechanical properties of some copolymer films were similar to those of commodity polymer films. The biodegradability and bioresistance of the copolymers depended on their chemical structure. All the investigated copolymers may be biodegradable under favorable for fungi growth conditions. The mass loss of the copolymers was in the range of (4.24–20.49)% after three month exposure in soil. The combination of mechanical, thermal properties, swelling in different solvents, biodegradability, and bioresistance of the synthesized polymers suggest that they can find the commercial application in the production of the soft consumer goods, industrial plastics, or coatings of the long-term use.

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