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Thermal decomposition of the copolymers based on long-chained diol dimethacrylates and BIS-GMA/TEGDMA

Krzysztof Pielichowski*, Dariusz Bogdał, Jan Pielichowski, Adam Boroń

Department of Chemistry, Technical University, ul. Warszawska 24, 31-155 Kraków, Poland

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Abstract

The process of thermal decomposition of copolymers based on six long-chained diol dimethacrylates, namely 1,4-butane-, 1,5-pentane-, 1,6-hexane-, 1,8-octane-, 1,10-decane- or 1,12-dodecanediol dimethacrylates (1,4-BDDM, 1,5-PDDM, 1,6-HDDM, 1,8-ODDM, 1,10-DDDM or 1,12-DDDDM, respectively), and 2,2-*bis*[4-(2-hydroxy-3-methacryloyl-oxypropoxy)phenyl]propane (BIS-GMA) or triethylene glycol dimethacrylate (TEGDMA), has been investigated by thermogravimetric analysis (TGA), TGA coupled with Fourier transform infra-red spectroscopy (TGA/FT–IR) and differential scanning calorimetry (DSC). It has been found that the polymers under investigation are thermally stable up to ≈250°C, as shown by the initial decomposition temperature (IDT) and that degradation profiles are generally of a one-step type. No post-cure effects were found on the basis of DSC scans, thus indicating formation of an infusible three-dimensional network. The qualitative and quantitative analysis of the main volatile products by TGA/FT–IR made it possible to confirm a polyesters' thermal degradation scheme with formation of CO_2, olefins and carbonyl-containing structures. © 1997 Elsevier Science B.V.

Keywords: Copolymers; Diol dimethacrylates; Thermal decomposition

1. Introduction

Many useful polymers consist of interconnected chains that form an infusible three-dimensional network whose formation is affected through numerous factors [1–3]. Improved structural materials, based on crosslinked systems, can be classified into four types:

1. the first two types deal with small-molar mass species. The first one corresponds to different functional end groups attached to small monomers, which leads to highly crosslinked networks. The second one corresponds to networks formed by chain copolymerization of di- and multifunctional monomers, which leads to a crosslink density controlled by the relative amount of each monomer.
2. the last two types deal with high-molar mass prepolymers. Either the crosslink is involved by the chain ends and in this case the crosslink density is directly related to the molar mass of the prepolymer, or the crosslink is due to the presence of curing agents whose amount controls the molar mass between crosslinks [4].

Depending on the macromolecular structure introduced by multifunctional monomers, different phase arrangements may occur, thus essentially influencing

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*Corresponding author. Fax: 0048 12 6342425.

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the thermal parameters. They are usually studied, in terms of stability, by means of thermogravimetric analysis (TGA). Much more meaningful information is available on the thermal degradation of polymers using hyphenated techniques, e.g. TGA coupled with Fourier transform infrared spectroscopy (TGA/FT–IR). This technique provides continuous monitoring of the IR spectra of evolving volatile products in function of temperature with on-time measurement of sample's weight loss. It offers some advantages over other analytical techniques, like flash or direct pyrolysis–mass spectrometry (Py or DPy-MS) or thermal volatilisation analysis (TVA), by making it possible to operate at modest, controlled temperatures and heating rates. This is crucial since at high temperatures organic polymers usually undergo complete thermal degradation and only low-molecular weight fragments are obtained. In fact, in the mass spectrum of a polymer, the molecular ions of the thermal products will appear mixed with the fragment ions formed in the ionizing step [5]. This makes it difficult to deduce a degradation pathway. On the other hand, in the sealed tube the products of degradation are retained within a constant volume and may undergo secondary reactions while in a TGA experiment they are flushed out with the purge gas and the possibility of recombination is greatly reduced [6]. Again, this makes it difficult to infer a degradation route.

The aim of this work was to investigate the thermal properties of the novel copolymers based on several long-chained diol dimethacrylates and BIS-GMA/TEGDMA as prospective candidates for numerous industrial applications, such as thermally-stimulated filling connectors and micro-scaled switch hose couplings, since they are characterized through a reasonably low shrinkage, as it had been described in a previous article [7].

2. Experimental

2.1. Materials

2.1.1. Synthesis of monomers

Diol dimethacrylates and triethylene glycol dimethacrylate were obtained in one-step reaction by a direct esterification. A 250 cm^3 three-necked bottomed flask, fitted with an efficient mechanical stirrer, a thermometer and a Dean–Stark's trap with a reflux condenser was charged with *n*-alkyl diol (0.25 mol), fresh distilled methacrylic acid (0.5 mol), hydroquinone (1 g), 96% H_2SO_4 (2 cm^3) and *n*-heptane (50 cm^3). The reaction vessel was placed in a heating mantle and refluxed until the quantitative amount of water was collected in the Dean–Stark's trap (3–6 h). The product was cooled and the solvent was evaporated under vacuum. The raw ester was placed in a separate funnel and washed three times with a 10% solution of NaOH, and then twice with a distilled water. The final product was dried over magnesium sulphate. Yield: 68–81%.

The synthesis of BIS-GMA was carried out in three-necked round bottomed flask with an efficient mechanical stirrer, a thermometer and a condenser. A fresh distilled methacylic acid, 95% diglycidyl ether bisphenol-A (in the stoichiometric proportions), 100 ppm hydroquinone and 1% by weight of N,N-dimethyl-*p*-toluidine as a catalyst were placed in the flask. The mixture was heated up to 60°C. The reaction was carried out until the peak at 917 cm^{-1} in FT–IR spectrum (terminal epoxy group) almost disappeared. The final product was analyzed by FT–IR and NMR methods.

2.1.2. Polymerization

The mixture of monomers was cured in glass molds by the addition of 1% by weight benzoyl peroxide. The samples were heated up to 70, 85, 100, 120°C over a period of 4, 1, 1 and 2 h [8].

2.2. Techniques

DSC measurements were performed on a Netzsch DSC 200, operating in a dynamic mode. Sample of ca. 7 mg was placed in aluminium pan and sealed; heating rate of 10 K/min was employed. Prior to use the calorimeter was carefully calibrated with an indium standard; an empty aluminium pan was used as reference.

Thermogravimetric analysis was performed on a Derivatograph-C (MOM, Hungary) thermal analyzer, operating in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample weight ca. 10 mg, atmosphere: air, temperature range: 25–500°C.

Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy was carried out using a Perkin–Elmer 7 thermogravimetric analyzer (T_{start}=30°C, heating rate; 50 K min^{-1}, sample weight ca. 10 mg, nitrogen flow: 50 cm^3/min) and a Perkin–Elmer 1725X FT–IR spectrometer. The thermogravimetric analyzer and spectrometer were suitably coupled to enable the passage of evolved products from the furnace to the gas cell over a short path, to minimize secondary reaction or condensation on cell walls. Moreover, the experimental conditions have been chosen to ensure that the condensable products form a submicron aerosol mist. This size aerosol has two advantages: (i) the particles follow the gas stream lines, thus minimizing condensation, and (ii) the particles produce little scattering in the mid IR, so the condensable products can be analyzed online in the FT–IR cell.

3. Results and discussion

The copolymers under investigation are of general structure:

Description of the samples used in the course of this work is given in Table 1

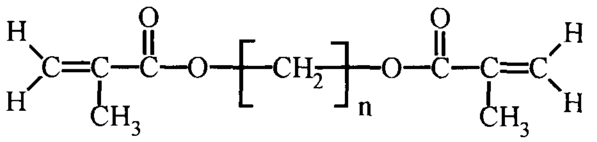
A 60 mol% BIS-GMA and 40 mol% TEGDMA copolymer was chosen as a primary system, to which other copolymers containing diol dimethacrylate are compared.

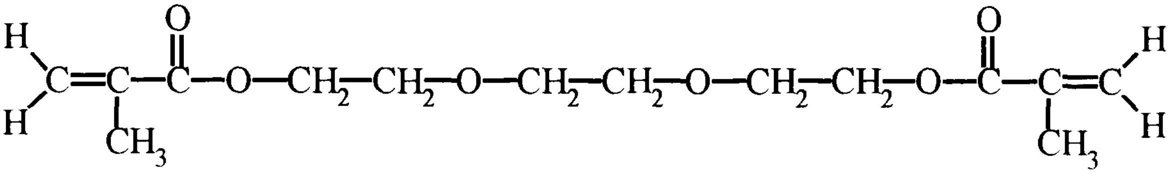
Results of the thermogravimetric analysis of copolymers based on 1,4-BDDM are presented in Fig. 1

It can be seen that copolymers are stable up to ≈270°C except of sample 1 which undergoes degradation at lower temperature of ≈240°C. Generally, decomposition proceeds in a one-step process, reaching its end at ≈500°C.

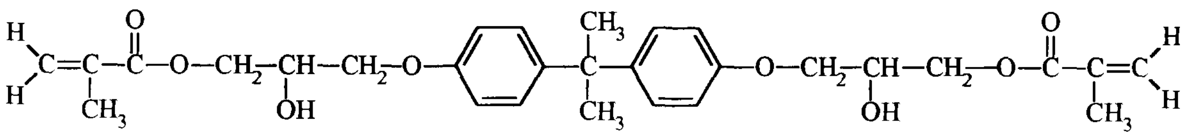
Copolymers containing 1,5-PDDM reveal a similar thermal behavior, with an IDT value of ≈270°C (Fig. 2); however, it should be noted that the IDT of sample 9 is shifted about 50°C towards higher temperatures.

For samples based on 1,6-HDDM typical one-step decomposition profiles were found. IDT values are in the 250–270°C range and some differences can only be seen for temperatures of mass loss 30, 50 and 70% (Fig. 3).





TEGDMA



BIS-GMA

Table 1
Description of the samples

Sample	BIS-GMA (%mol)	TEGDMA (%mol)	1,4-BDDM (%mol)	1,5-PDDM (%mol)	1,6-HDDM (%mol)	1,8-ODDM (%mol)	1,10-DDM (%mol)	1,12- DDDDM (%mol)
1	60	40	0	0	0	0	0	0
2	60	30	10	0	0	0	0	0
3	60	20	20	0	0	0	0	0
4	60	10	30	0	0	0	0	0
5	60	0	40	0	0	0	0	0
6	60	30	0	10	0	0	0	0
7	60	20	0	20	0	0	0	0
8	60	10	0	30	0	0	0	0
9	60	0	0	40	0	0	0	0
10	60	30	0	0	10	0	0	0
11	60	20	0	0	20	0	0	0
12	60	10	0	0	30	0	0	0
13	60	0	0	0	40	0	0	0
14	60	30	0	0	0	10	0	0
15	60	20	0	0	0	20	0	0
16	60	10	0	0	0	30	0	0
17	60	0	0	0	0	40	0	0
18	60	30	0	0	0	0	10	0
19	60	20	0	0	0	0	20	0
20	60	10	0	0	0	0	30	0
21	60	0	0	0	0	0	40	0
22	60	30	0	0	0	0	0	10
23	60	20	0	0	0	0	0	20
24	60	10	0	0	0	0	0	30
25	60	0	0	0	0	0	0	40

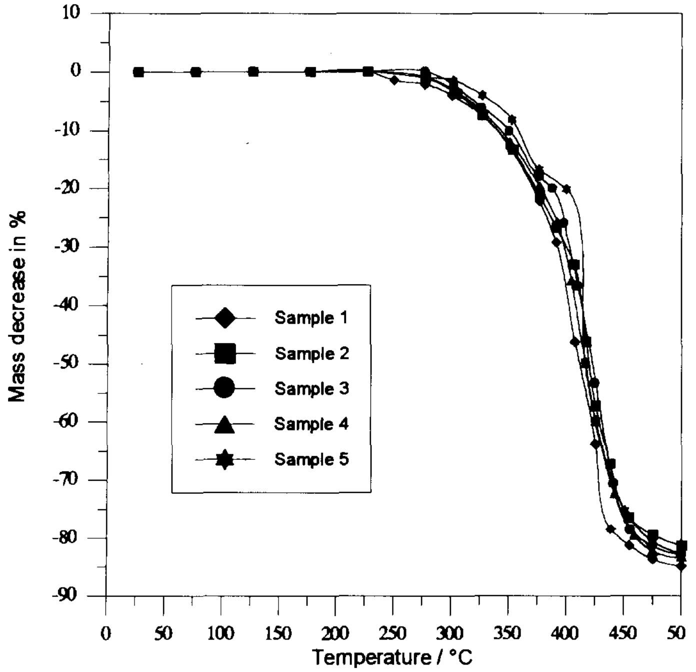


Fig. 1. TGA scans at 10 K/min of samples 1–5.

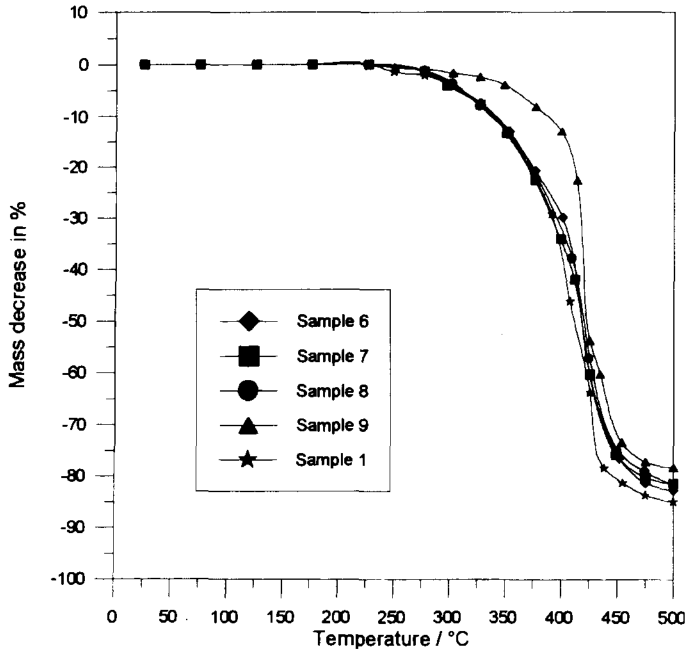


Fig. 2. TGA scans at 10 K/min of samples 6–9.

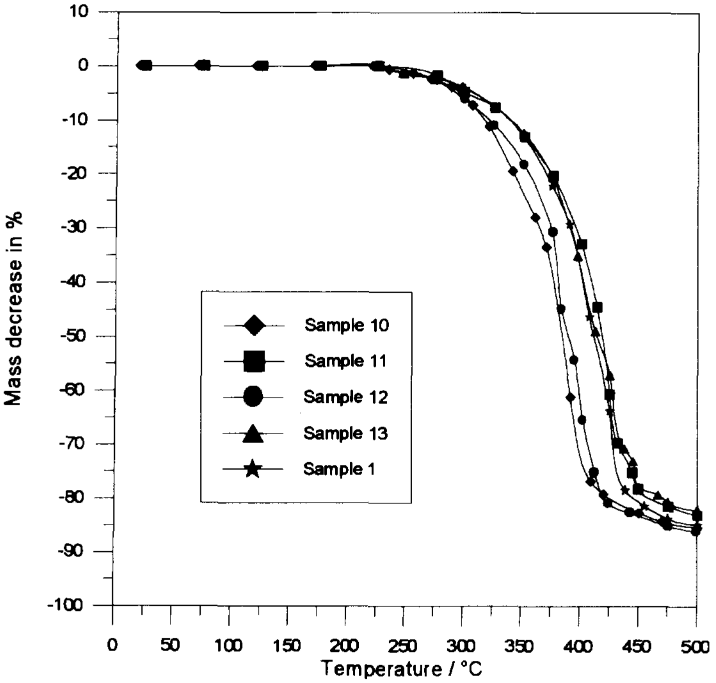


Fig. 3. TGA scans at 10 K/min of samples 10–13.

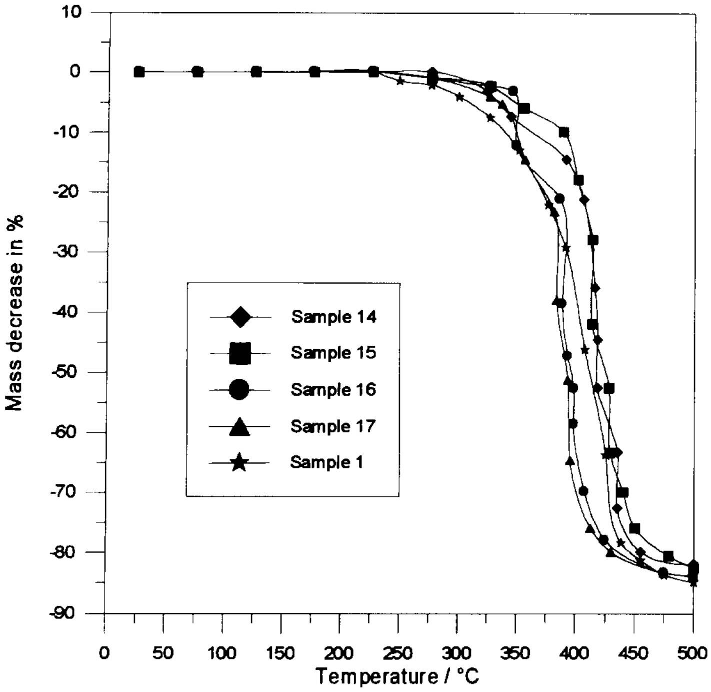


Fig. 4. TGA scans at 10 K/min of samples 14–17.

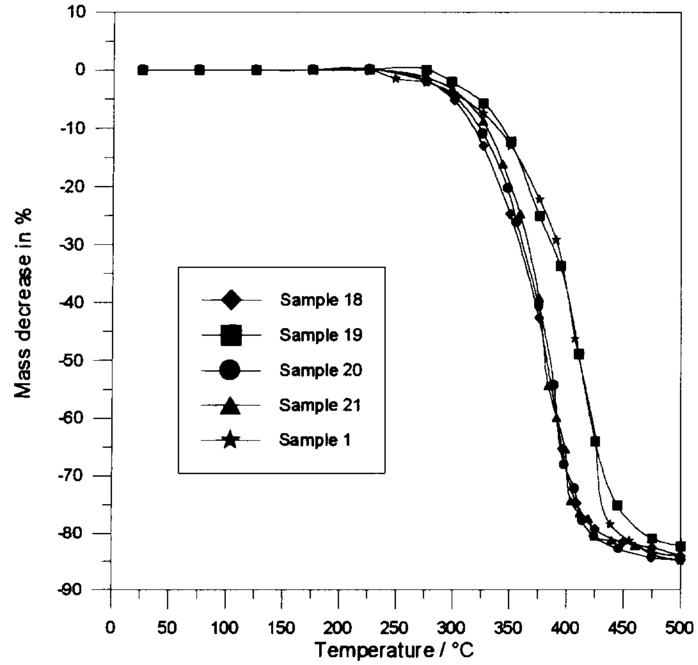


Fig. 5. TGA scans at 10 K/min of samples 18–21.

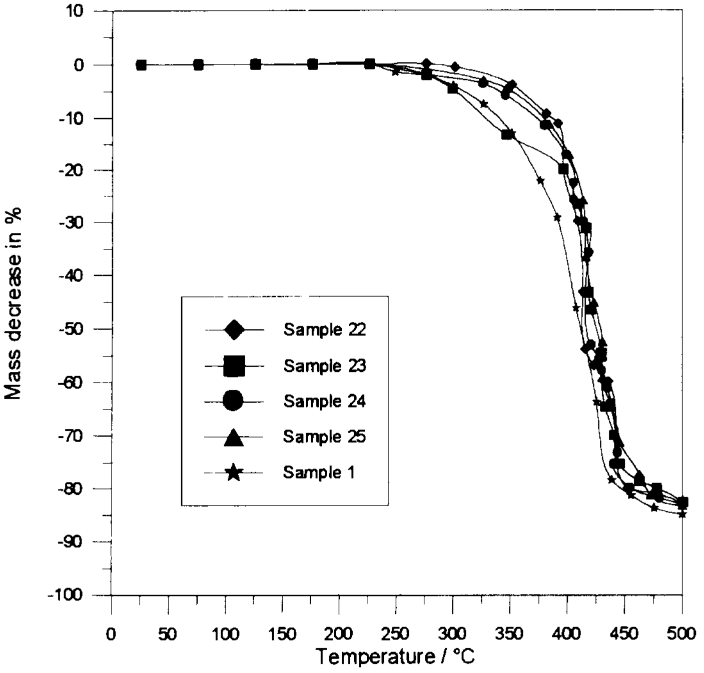


Fig. 6. TGA scans at 10 K/min of samples 22–25.

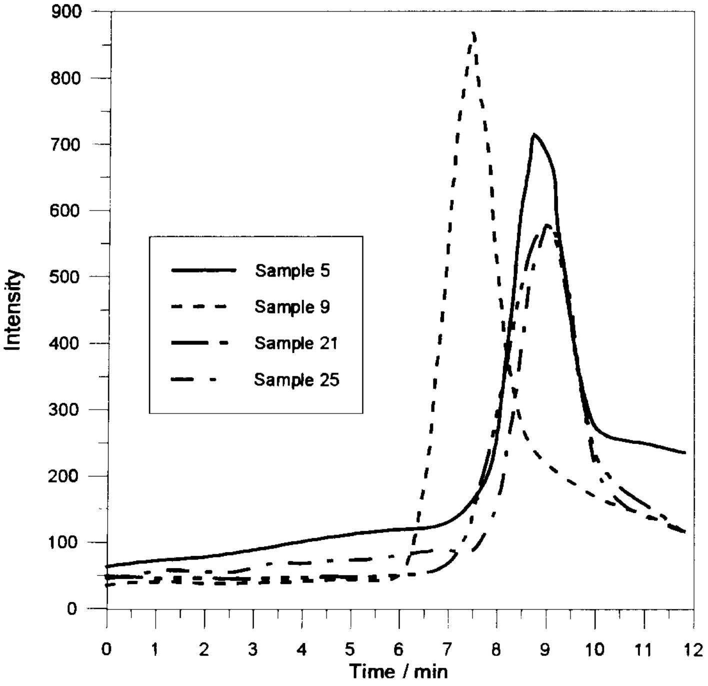


Fig. 7. Gram–Schmidt chromatograms of samples 5, 9, 21 and 25.

Thermogravimetric scans of samples 14–17 with 1,8-ODDM show that they are more thermally stable than the primary BIS-GMA/TEGDMA system. For sample 15 the difference in IDT value reaches its maximal value of ≈50°C, as shown in Fig. 4. Similar observations can be made for copolymers of 1,10-DDDM; for this series of samples resin containing 20% mol of an appropriate diol proved to be the most thermally stable in terms of the IDT value (Fig. 5).

The last TGA analysis were done on samples based on 1,12-DDDDM (Fig. 6). It has been found that certain similarities with decomposition pathways of the samples with shorter spacers occur. The IDT value is still the lowest for a basic system – introduction of 1,12-DDDDM improve the value of this parameter for ≈50°C for sample 23.

On the basis of TGA measurements, it can be found that introduction of diol dimethacrylates cause an increase of the IDT value (up to 50°C) and slightly changes the overall decomposition scheme. This is due to the better sterical ability of diol dimethacrylates to form consistent three-dimensioned networks – regular macromolecular alignment results both in better thermal and mechanical properties and in relatively low shrinkage, thus making it possible to consider these materials for new applications. To gain a deeper look into the degradation mechanism TGA/FT–IR method was employed. Evolved gas profiles, obtained by the Gram–Schmidt orthogonalization, are of similar shape, indicating a one-step decomposition process (Fig. 7).

FT–IR spectra were recorded at the peak maximum temperature and additionally at higher temperature to determine the nature of the volatile degradation product(s). As indicated in Fig. 8, the gaseous products to evolve from the degrading polymer appear to contain the OH (ca. 3600 cm^{-1}), CH (ca. 3050 cm^{-1}), CO_2

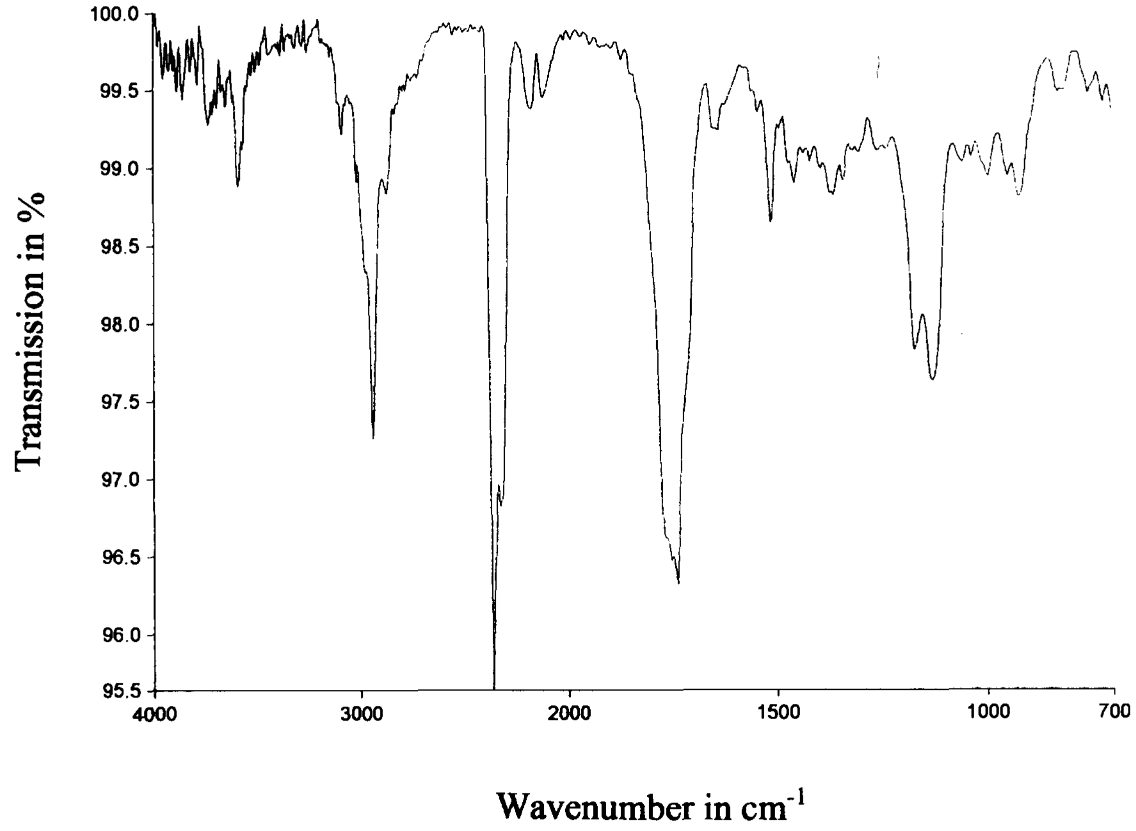


Fig. 8. FT–IR spectrum of sample 9 after 7.5 min.

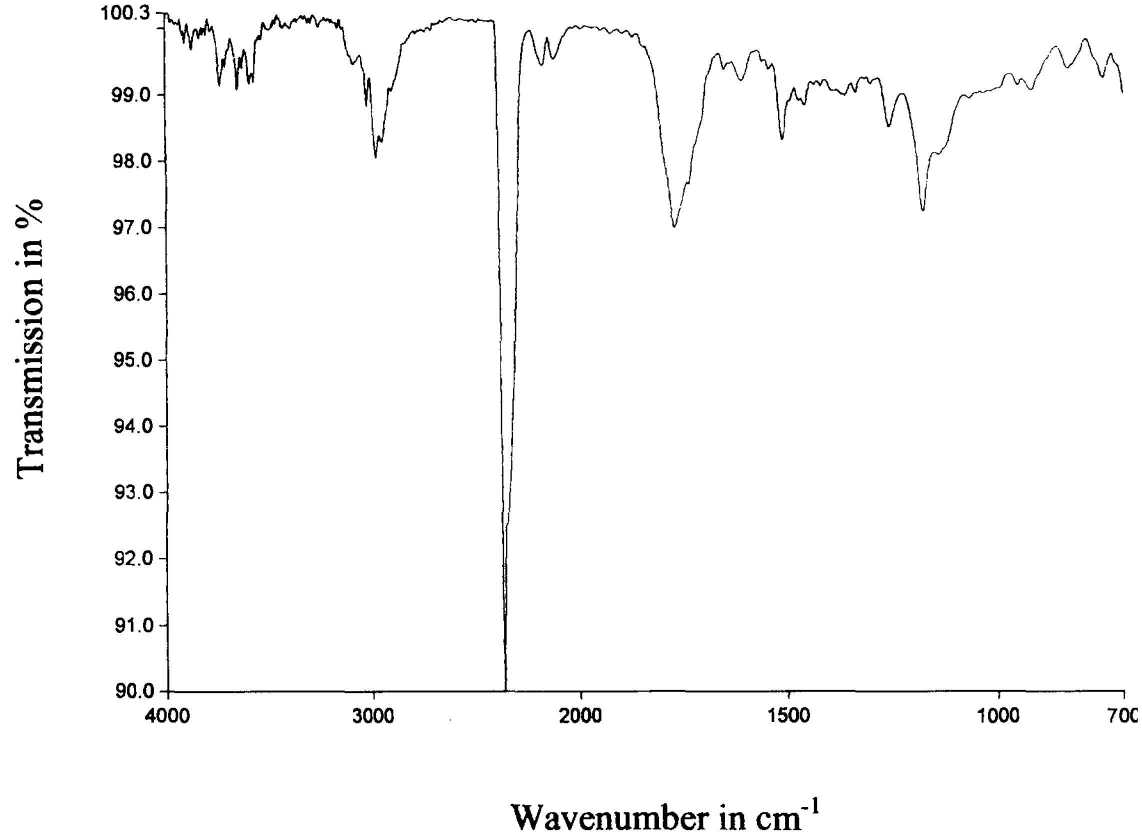


Fig. 9. FT–IR spectrum of sample 9 after 9.0 min.

(ca. 2470 cm^{-1}), C=O (ca. 1750 cm^{-1}), C–O (ca. 1200 cm^{-1}) and olefinic CH groups (ca. 910 cm^{-1}). The spectrum describing next degradation region is shown in Fig. 9.

Evolution of volatiles can be easily followed by analysis of FT–IR spectra displayed in form of a stacked plot (Fig. 10)

TGA/FT–IR results indicate in the degradation mechanism, typical for polyester systems. It eventually leads to the formation of olefines, CO_2, carbonyl-containing structures and proceeds mostly via a radical route [9]. It is expected that this radical mechanism shall be supported in the presence of oxygen because of its (bi)radical nature.

DSC studies were performed to evaluate the heat effects occurring while the sample is subjected to a controlled heating program. It has been found that no post-cure effects take place, as shown in several examples in Fig. 11, thus indicating that cure was completed during polymerization.

Crosslinking process seems to have made the polymeric network too immobile for any significant physical or chemical changes to occur in this temperature range.

4. Conclusions

We synthesized a series of long-chained diol dimethacrylates, which were further copolymerized in different molar ratios with BIS-GMA to replace the traditionally used TEGDMA monomer. Using TGA and TGA/FT–IR methods we were able to determine the relative thermal stability of the copolymers and evaluate the influence of the kind and amount

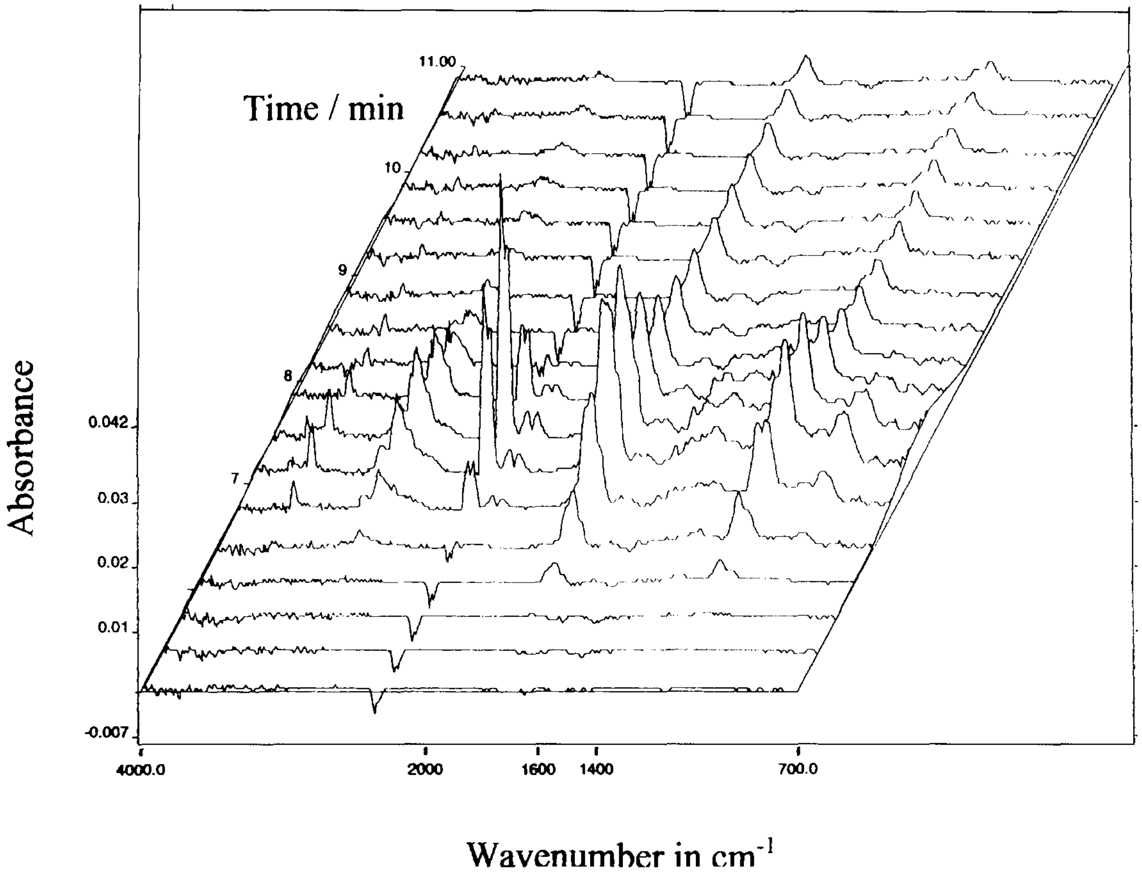


Fig. 10. Stacked plots of FT/IR spectra of sample 5 from 0–11 min.

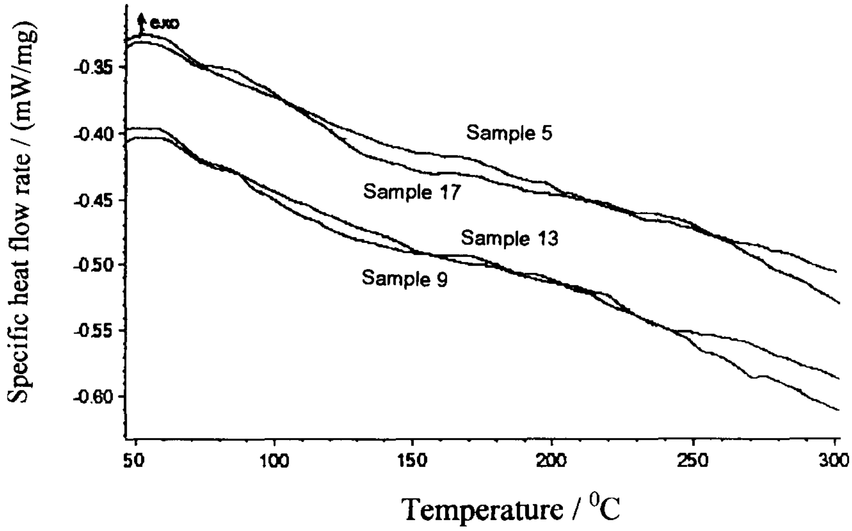


Fig. 11. DSC scans at 10 K/min of samples 5, 9, 13 and 17.

of diol dimethacrylates on the IDT. We found that introduction of diol dimethacrylate into copolymer structure may cause an increase of IDT value up to 50°C. By analysis of the TGA/FT–IR degradation results of these fully cured, three-dimensional networks (as indicated by DSC data), we come to conclusion that the systems under investigation are governed by thermal mechanisms typical for polyester systems.

Acknowledgements

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