Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Characterization of 2-Hydroxyethyl Methacrylate (HEMA) and Methyl Methacrylate (MMA) Copolymer Used as Biomaterial

Elif Vargün[a][b]; Mehmet Sankir[c]; Bengi Aran[a][c]; Nurdan D. Sankir[c]; Ali Usanmaz[a]
[a] Polymer Science and Technology, Department of Chemistry, Middle East Technical University, Ankara, Turkey [b] Department of Chemistry, Mugla University, Mugla, Turkey [c] Nanotechnology and Membrane Science Laboratory, TOBB University of Economics and Technology, Ankara, Turkey

To cite this Article Vargün, Elif , Sankir, Mehmet , Aran, Bengi , Sankir, Nurdan D. and Usanmaz, Ali(2010) 'Synthesis and Characterization of 2-Hydroxyethyl Methacrylate (HEMA) and Methyl Methacrylate (MMA) Copolymer Used as Biomaterial', Journal of Macromolecular Science, Part A, 47: 3, 235 — 240

To link to this Article: DOI: 10.1080/10601320903526998

URL: http://dx.doi.org/10.1080/10601320903526998

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2010) **47**, 235–240
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903526998

Synthesis and Characterization of 2-Hydroxyethyl Methacrylate (HEMA) and Methyl Methacrylate (MMA) Copolymer Used as Biomaterial

ELİF VARGÜN[2,3], MEHMET SANKIR[1], BENGİ ARAN[1,2], NURDAN D. SANKIR[1] and ALİ USANMAZ[2,*]

[1] *Nanotechnology and Membrane Science Laboratory, TOBB University of Economics and Technology, Sogutozu Ankara, Turkey*
[2] *Polymer Science and Technology, Department of Chemistry, Middle East Technical University, Ankara Turkey*
[3] *Department of Chemistry, Mugla University, Mugla, Turkey*

Received August 2009, Accepted September 2009

A series of poly(methyl methacrylate-co-hydroxyethyl methacrylate) (PMMA-co-PHEMA), copolymers were synthesized by an emulsion polymerization technique. Copolymer compositions were determined by FT-IR and ^{1}H-NMR spectroscopy. It was found that comonomer ratios used in the recipes were comparable within the actual copolymers. Glass transition temperatures (T_g) of PMMA-co-PHEMA copolymers were varied from 119°C to 100°C by increasing HEMA content. Thermogravimetric analysis showed that the copolymers were stable up to 330°C. High intrinsic viscosity values of copolymer resulted in ductile solution-cast films. The hydrophilicity of the films was analyzed by water uptake measurements.

Keywords: Methyl methacrylate, hydroxyethyl methacrylate, emulsion polymerization, copolymers, equilibrium swelling ratio

1 Introduction

Poly(methyl methacrylate), PMMA, and poly(2-hydroxyethyl methacrylate), PHEMA, are the most common members of the methacrylic acid ester polymers. Due to its good optical (high transparency and clarity) and mechanical properties, PMMA has been used in a wide range of fields such as biomaterials, optoelectronics and optic fibers (1). On the other hand, polymeric hydrogel, PHEMA, also has great interest owing to its hydrophilicity, mainly from the hydroxyl functional group. Hence, PMMA has been copolymerized with HEMA to tailor the hydrophilicity and wettability of PMMA which can then be used in some special applications, particularly, in solid-state pulsed dye lasers (2–5) and in biomedical fields (6–10). The poly(MMA-co-HEMA) copolymers have been synthesized by suspension and microemulsion systems (11–14). However, the conventional emulsion polymerization is an efficient and versatile technique using non-toxic medium. It also offers to the well-defined polymers of different functional methacrylic esters.

PHEMA is the most widely used hydrogel since the water content is similar to living tissues. Also, it has bio- and blood-compatibility and shows resistance to degradation and can be in different shapes and forms (15–17). Moreover, PHEMA based soft contact lenses and intraocular lenses are the most important application area of this polymer due to high oxygen permeability, good mechanical properties and favorable refractive index value (18,19). It is very crucial to tailor the swelling behavior of such an important biopolymer to utilize them in pharmaceutical and medical research. In this study, we synthesized PMMA-co-PHEMA copolymers to mainly control both hydrophilicty and glass transition temperatures. Besides the chemical and thermal characterization, swelling behaviors of the copolymer films were studied.

2 Experimental

2.1 Materials

MMA (99%, Acros Organics) and HEMA (98%, Acros Organics) were distilled under reduced pressure prior to use. Ammonium persulfate initiator (APS, 99+%, Acros Organics) and 1-dodecanthiol chain transfer agent (98%, Merck) were used as received. DOWFAX 8390 was used as a surfactant without further purification. Magnesium

---

*Address correspondence to: Alı Usanmaz, Department of Chemistry and Polymer Science and Technology, Middle East Technical University, Ankara, Turkey. Tel: 90-312-2103225; Fax: 90-312-2103200; E-mail: usanmaz@metu.edu.tr

Table 1. Recipes for PHEMA and PMMA-co-PHEMA synthesis

Acronym	*MMA (g)*	*HEMA (g)*	*Surfactant (g)*	*APS (g)*	*1-dodecanthiol (g)*	*Water (mL)*
PHEMA	–	22.13	1.77	0.0221	0.4205	42
*PMMA(95) -co PHEMA(5)	22.06	5.06	1.89	0.0236	0.4479	52

*A typical copolymer including 95 molar percent of MMA and 5 molar percent HEMA.

sulfate ($MgSO_4$, 97%, Acros Organics) and N,N-dimethyl formamide (DMF, 99.8%, Acros Organics) were used as received. Deionized water (18.2 $m\Omega.cm^{-1}$) was used throughout the experiments.

2.2 Synthesis of PMMA-co-PHEMA and PHEMA

A 250 mL flask was charged with a mechanical stirrer, condenser, thermocouple, dropping funnel and nitrogen inlet. The temperature was raised to 65°C and the flask was purged with nitrogen for an hour. The surfactant, initiator (65% of total initiator) and mercaptan were added, followed by the premix of the monomer mixture (20% of total monomer). The remaining monomer mixture was added dropwise for 2 h. Then, the remaining initiator was added to the flask and stirred for additional 30 min. The copolymers were precipitated with 1% aqueous $MgSO_4$ solution and the filtrate was washed with distilled water several times. The product was dried in a vacuum oven at 60°C overnight. Table 1 shows the recipe for polymerization.

2.3 Film Preparation and Swelling Test

An appropriate amount of copolymers (usually 5 wt%) were dissolved in DMF and the solution was cast on a smooth glass plate. Excess solvent was removed under the IR lamp. Films were further dried at 60°C for 24 h prior to the characterizations. The dry film samples were cut into a square shape with fixed dimension and weighed carefully, then kept in a vial.

2.4 Characterization

The ^1H-NMR spectra of the synthesized samples were recorded in d_6-DMSO and deuterated chloroform using an Ultrashield 400 MHz Digital NMR Bruker spectrometer. The dry polymers were mixed with KBr and pressed into a pellet and FT-IR spectra were then obtained with a Bruker Vertex-70 FT-IR spectrometer. Viscosities of the polymer solutions (with a concentration of 0.2 g/20 mL) were measured with a capillary Ubbelohde viscometer in 1-methyl 2-pyrolidinone at 30°C. TGA thermograms were taken on Perkin-Elmer Pyris 1 TGA under nitrogen atmosphere and the polymer was heated from 35°C to 500°C with a heating rate of 10°C/min. Differential scanning calorimetry DSC was performed with a Perkin-Elmer Diamond DSC under N_2 atmosphere with a heating rate of 10°C/min. An Instron 3361 Tensile Testing Machine with a constant extension rate of 10 mm/min was used to obtain the tensile data of copolymers. The Digital Abbe Refractometer

Table 2. Compositions obtained from ^1H-NMR data, intrinsic viscosities, 10% weight loss temperatures and WU data of the copolymers

Comonomers in feed (mol%)[a]	*Comonomers in polymer (molar percent) MMA/HEMA*[b]	$[\eta]^{30^\circ C}_{NMP}$	T_{10} *(°C)*	*% SR*
PMMA(95)-co-PHEMA(5)	94.9 / 5.1	0.5	323	1.2
PMMA(90)-co-HEMA(10)	90.2 / 9.8	2.4	285	1.9
PMMA(85)-co-HEMA(15)	84.5 / 15.5	1.1	316	4.1
PMMA(80)-co-HEMA(20)	79.7 / 20.3	1.5	319	6.9
PMMA(70)-co-HEMA(30)	68.1 / 31.9	0.9	310	7.5
PMMA(50)-co-HEMA(50)	40.9 / 59.1	0.3	316	13.4

[a] By weight.
[b] By proton NMR.

Table 3. The tensile properties of PMMA-co-PHEMA copolymers

Sample	*Ultimate Tensile Strength (MPa)*	*Young's Modulus(MPa)*	*Elongation at Break (%)*
PMMA(95)-co-PHEMA (5)	31.13 ± 1.49	1.36 ± 0.09	32.27 ± 1.47
PMMA(90)-co-PHEMA(10)	29.61 ± 0.43	1.36 ± 0.08	28.83 ± 2.91
PMMA(85)-co-PHEMA(15)	23.12 ± 0.46	1.35 ± 0.11	21.12 ± 3.02
PMMA(80)-co-PHEMA(20)	18.19 ± 0.82	1.12 ± 0.06	18.77 ± 1.79

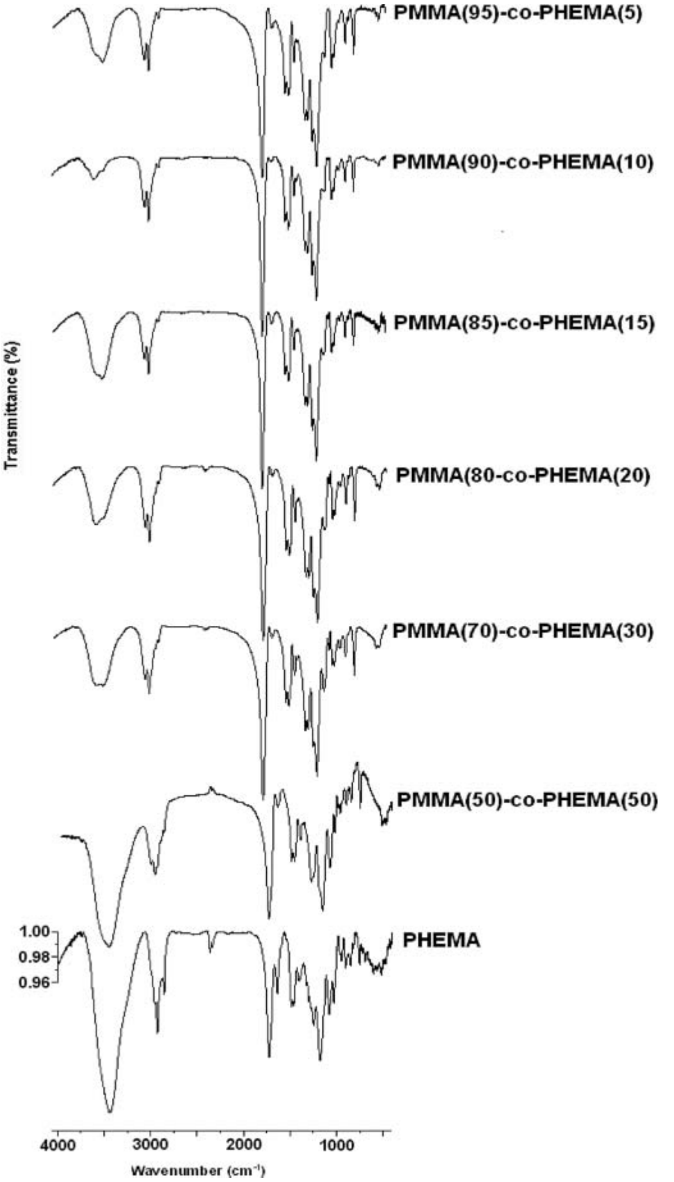

Fig. 1. FT-IR spectra of PHEMA and PMMA-co-PHEMA copolymers.

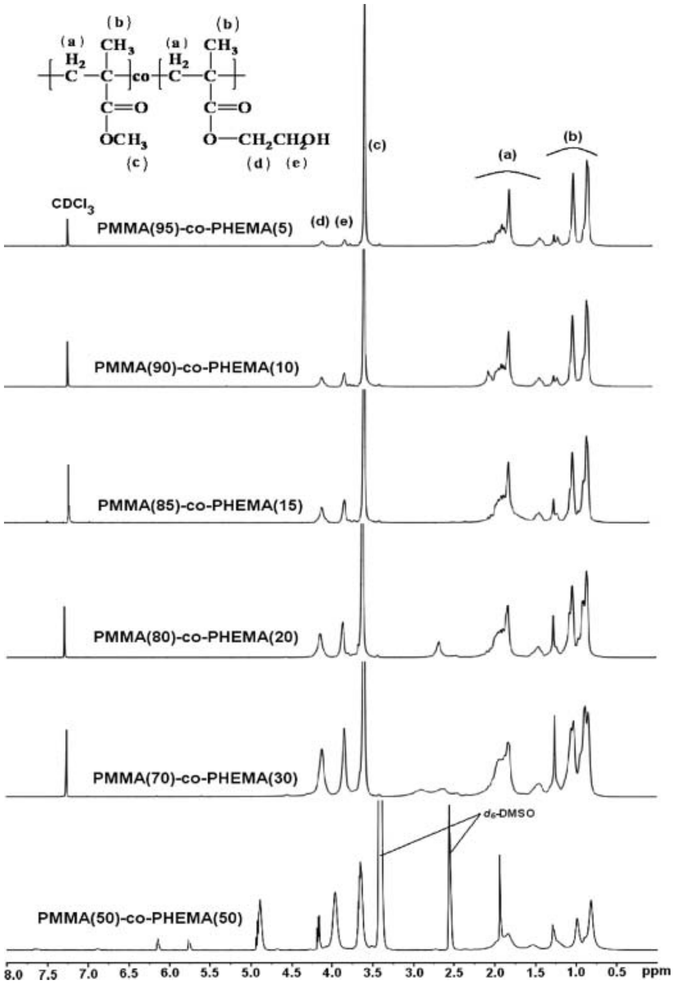

Fig. 2. ^{1}H-NMR spectra of PMMA-co-PHEMA copolymers from 95/5 to 50/50 mol%.

DR-A1 instrument was also used for the refractive index measurements of the different HEMA containing copolymers. Swelling behavior of the PMMA-PHEMA copolymers with various HEMA content have also been studied. Polymer films were immersed into the water at room temperature until swelling equilibrium was attained. The weight gain of the films was recorded at a function of time. The equilibrium swelling ratio (SR) of films was calculated using the following Equation 1:

$$\mathrm{SR(wt\%)} = \frac{\mathrm{Ww} - \mathrm{Wd}}{\mathrm{Wd}} \times 100 \tag{1}$$

Where W_w is the weight of the wet sample at equilibrium and W_d is the weight of a fully dried sample. Time dependency of the sorbed water was used to determine the dynamic swelling behavior of the films.

The following Equation 2 can be used to calculate the degree of swelling (q):

$$q = \frac{W_t}{W_o} \tag{2}$$

Where W_t is the weight of the swollen film at time t and W_0 is the weight of film at time 0.

Table 4. The variation of refractive index of PMMA-co-PHEMA copolymers with different compositions

Sample	*Refractive index*	*Temp. (°C)*
PMMA(95)-co-PHEMA (5)	1.4073	21.4
PMMA(90)-co-PHEMA(10)	1.3547	21.5
PMMA(85)-co-PHEMA(15)	1.3852	21.3
PMMA(80)-co-PHEMA(20)	1.3166	21.7
PMMA(70)-co-PHEMA(30)	1.4418	21.5
PMMA(50)-co-PHEMA(50)	1.4057	21.7

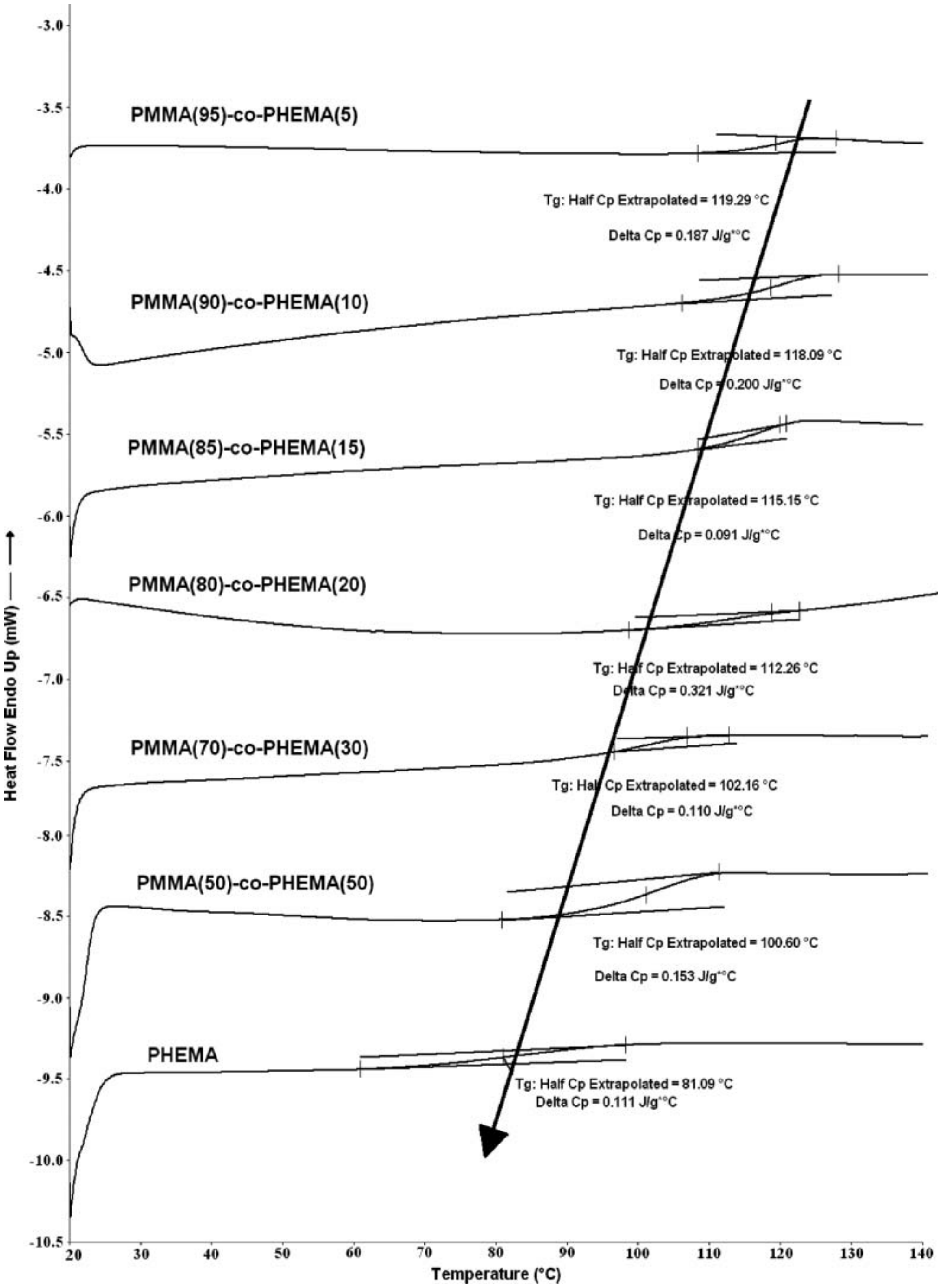

Fig. 3. DSC curves of PMMA-co-PHEMA copolymers from 95/5 to 50/50 molar ratios and PHEMA homopolymer.

3 Results and Discussion

Chemical structure of both homo and copolymers were identified with several techniques. The FT-IR spectra of PHEMA homopolymer and six different compositions of P(MMA-co-HEMA) copolymers are given in Figure 1. The characteristic carbonyl –C=O stretching in both MMA and HEMA units in the copolymer arises at 1732 cm^{-1}. –CH_3 and –CH_2 stretching vibrations appeared around 2953 cm^{-1}. The strong band at 1450 cm^{-1}can be assigned –CH bending and -C-O-C- type ester stretching at around 1280–1057 cm^{-1}. The wide and intense peak at 3444 cm^{-1} due to the -OH stretching increasing with the HEMA content in the copolymers was an obvious characteristic peak of the series.

The ^{1}H-NMR spectra of PMMA-co-PHEMA copolymers at various molar percent of HEMA from 5 to 50% are given in Figure 2. Since the PMMA(50)-co-PHEMA(50) composition was insoluble in deuterated chloroform due to the increasing hydrophilic character of the copolymer, it was dissolved in d_6-DMSO. On the other hand, other copolymer series were soluble in deuterated chloroform. The methyl protons for the ester group in MMA units appear at 3.6 ppm (c). Signals at 0.9–1.3 ppm can be asssigned to the α-CH_3 protons (b) in both MMA and HEMA units. Methylene protons (a) ranged between 1.4–2.1 ppm and the signals at 4.2 and 3.9 pmm corresponds to the –OCH_2 (d) and –CH_2OH (e) protons, respectively. Copolymer compositions from proton NMR were calculated by the integral area (I) of the –OCH_3(c) and –OCH_2(d) protons using the following Equation 3 (Table 2). ^{1}H-NMR data confirmed that the copolymer compositions were agreed with the charged monomer feed.

$$\text{Mol percent of HEMA} = \frac{1d/2}{1d/2 + 1c/3} \times 100 \qquad (3)$$

MMA was copolymerized with HEMA up to 30% in the literature (16). In this study, the incorporation of HEMA into the copolymers was achieved up to 50 molar percent with a relatively lower intrinsic viscosities (IV). However, IV values of the copolymers were quite enough for ductile film forming. Once higher than 50 molar percent of HEMA was used for copolymerization, the resulting polymer ended up with mostly homopolymerization of HEMA.

Glass transition temperatures of copolymers were decreased from 119°C to 100°C with an increasing amount of HEMA (Fig. 3). The T_g of PMMA is lowered by copolymerization with HEMA, which may ease the processing conditions. This could be important data which one would try heat processing of these copolymers.

Thermal stabilities of the synthesized copolymers were determined by thermogravimetric analysis (TGA) (Fig. 4). The decomposition temperatures of copolymers are in the range of 330–371°C. It is found that the thermal degradation temperatures of the copolymers shifted to the higher value with incorporation of HEMA. This can be seen at 10 wt% loss temperatures of copolymers (Table 2). TGA results confirmed that the PMMA-co-PHEMA copolymers are thermooxidatively stable up to 330°C.

Equilibrium swelling data of copolymer films in water at room temperature can be seen in Table 2. Since HEMA introduces more hydrophilic functional groups into the copolymers, as expected the water uptake of the films were increased from 1.2 to 13.4% when the HEMA content was increased from 5 to 50 molar percent. Table 2 also reveals that controlling the hydrophilicity by a single step copolymerization with suitable comonomers was achieved. This could be very beneficial in pharmaceutical and medical research where tailoring the swelling behavior of these materials is vital.

Variation of the degree of swelling (q) with HEMA content in the copolymer can be seen in Figure 5. As expected, the degree of swelling decreased with decreasing the HEMA content. An overshooting phenomenon has been observed for all PMMA-PHEMA copolymers. This behavior basically means that copolymers exhibit a maximum degree of swelling following by a gradually decrease until the equilibrium is attained. Similar swelling behavior of the hydrogel containing copolymers has been discussed in the literature (21–23). Overshooting behavior of PMMA-PHEMA copolymers could be attributed to the polymer network relaxation. Initially copolymers absorb more water, since the diffusion of water is faster in the hydrogel part (HEMA) compared to the PMMA chain. Then, when the copolymer relaxes to equilibrium conformation, films expel some water.

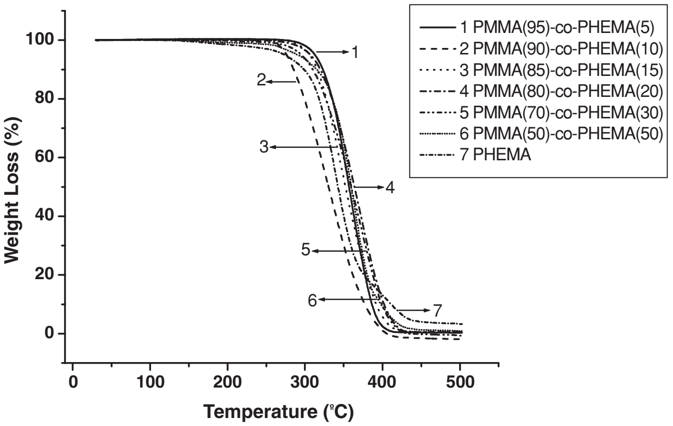

Fig. 4. TGA thermogram of PMMA-co-PHEMA copolymers and PHEMA homopolymer; all samples are thermooxidatively stable.

Table 3 presents the tensile data for the series of copolymers and the PMMA(95)-co-PHEMA (5) copolymer has the highest modulus and strength values compared to other copolymer compositions. A decreasing trend is observed in

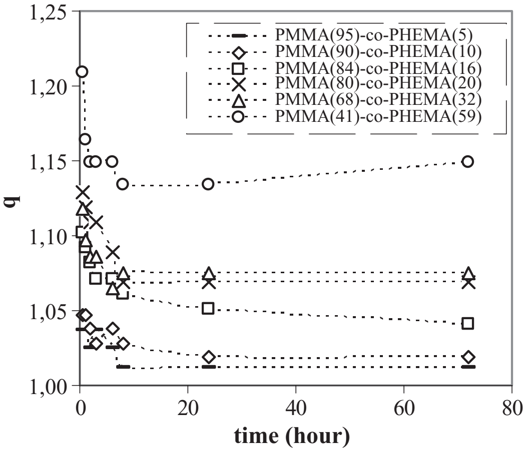

Fig. 5. Degree of swelling vs. time curves for various PMMA-co-PHEMA copolymers.

elongation at break while increasing the HEMA content in copolymers.

The glassy and amorphous PMMA has a refractive index of around 1.49 (20) and the different refractive index values for the different PHEMA containing copolymers are shown in Table 4. Even though the refractive indexes of the samples fluctuated by copolymerization with hydroxyl functionalized methacrylate polymer, the values are close to each other showing similar optical properties.

4 Conclusions

Thermooxidatively stable and ductile film forming copolymers were successfully synthesized by emulsion copolymerization. Chemical structure and compositions were identified by FTIR and ^{1}H-NMR spectroscopy. The glass transition temperatures of copolymers were controlled from 119°C to 100°C. Controlling glass transition temperatures could be important data while melt processing of these copolymers. Degree of swelling was also tailored by single step copolymerization. As expected, water uptake measurements showed that the copolymers absorbed more water with the incorporation of HEMA. Copolymers were thermooxidatively stable up to 330°C. Overshooting effect has been observed for the swelling behavior of the PMMA-PHEMA copolymers. The degree of swelling of the all copolymers presented here increased up to a critical time. After a certain time, q values decreased and reached equilibrium due to the relation phenomenon of the polymer network. Moreover, it has been observed that, degree of swelling increased with increasing the PHEMA content.

Acknowledgements

Financial support from The Scientific and Technological Research Council of Turkey under the contract #108T099 is gratefully acknowledged. The authors thank to Middle East Technical University Central Laboratory for DSC and TGA analysis.

References

1. Ernest, A.D. and Lamb, D.W. (2005) *Journal of Phys: Conf. Series*, 15, 270–275.
2. Susdorf, T., Del Agua, D., Tyagi, A., Penzkofer, A., Garcia, O., Sastre, R., Costela, A. and Garcia-Moreno, I. (2007) *Appl. Phys. B*, 86, 537–545.
3. Abedin, K.M., Alvarez, M., Costela, A., Garcia-Moreno, I., Garcia, O., Sastre, R., Coutts, D.W. and Webb, C.E. (2003) *Optics Communications*, 218, 359–363.
4. Pons, M., Nonell, S., Garcia-Moreno, I., Costela, A. and Sastre, R. (2002) *Appl. Phys. B*, 75, 687–694.
5. Nonell, S., Marti, C., Garcia-Moreno, I., Costela, A. and Sastre, R. (2001) *Appl. Phys. B*, 72, 355–360.
6. Atai, M., Watts, D.C. and Atai, Z. (2005) *Biomaterials*, 26, 5015–5020.
7. Dalton, P. Flynn, D.L. and Shoichet, M.S. (2002) *Biomaterials*, 23, 3843–3851.
8. Bar, F.W., Van der Veen, F.H., Benzina, A., Habets, J. and Koole, L.H. (2000) *Journal of Biomed. Mater. Res.*, 52, 193–198.
9. Sivakumar, M. and Panduranga Rao, K. (2002) *Journal of Applied Polymer Science*, 83, 3045–3054.
10. Arimoto, M., Ichikawa, H. and Fukumori, Y. (2004) *Powder Technology*, 141, 177–186.
11. Denizli, A., Köktürk, G., Salih, B., Kozluca, A. and Pişkin, E. (1997) *Journal of Applied Polymer Science*, 63, 27–34.
12. Chieng,T.H., Gan, L.M., Chew, C.H. and Ng, S.C. (1995) *Polymer*, 36, 1941–1946.
13. Ayhan, H. (2002) *Journal of Bioactive and Compatible Polymers*, 17, 271–283.
14. Özer, F., Beşkardes, M.O., Zareie, H. and Pişkin, E. (2001) *Journal of Applied Polymer Science*, 82, 237–242.
15. Rayment, E.A., Dargaville, T.R., Shooter, G.K., George, G.A. and Upton, Z. (2008) *Biomaterials,* 29, 1785–1795.
16. Schiraldi, C., D'Agostino, A., Oliva, A., Flamma, F., De Rosa, A., Apicella, A. and De Rosa, R.M. (2004) *Biomaterials*, 25, 3645–3653.
17. Bhawal, S., Reddy, L.H., Murthy, R.S.R. and Devi, S. (2004) *Journal of Applied Polymer Science*, 92, 402–409.
18. Lee, S.D., Hsiue, G.H., Kao, C.Y. and Chang, P.C.T. (1996) *Biomaterials*, 17(6), 587–595
19. Karlgard,C.C.S., Sarkar, D.K., Jones, L.W., Moresoli, C. and Leung, K.T. (2004) *Applied Surface Science*, 230, 106–114.
20. Kasarova, S.N., Sultanova,N.G., Ivanov, C.D. and Nikolov, I.D. (2007) *Optical Materials* 29, 1481–1490.
21. Kabra, B.G., Gehrke, S.H., Hwang, S.T. and Ritschel,W.A. (1991) *Journal of Applied Polymer Science*, 42, 2409–2416.
22. Lee, W.F. and Lin, Y.H. (2001) *Journal of Applied Polymer Science*, 81, 1360–1371.
23. Yin, Y., Ji, X., Dong, H., Ying, Y. and Zheng, H. (2008) *Carbohydrate Polymers*, 71, 682–689.