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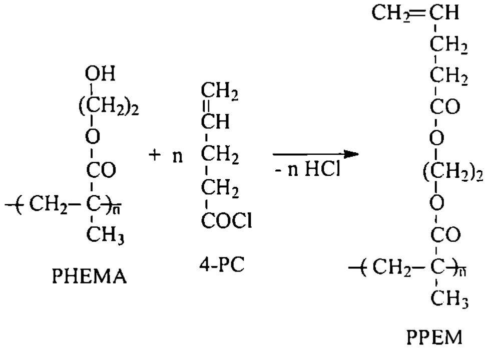
Preparation and characterization of poly[2-(4-pentenoyloxy)ethyl methacrylate]

Summary — A new multimonomer, the poly[2-(4-pentenoyloxy)ethyl methacrylate] (PPEM) has been synthesized by Schotten-Bauman's esterification of poly(2-hydroxyethyl methacrylate) with 4-pentenoyl chloride. Its chemical structure was confirmed by means of FTIR, ^{1}H NMR, ^{13}C NMR spectra as well as by elemental analysis. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were used to determine the thermal behavior of the PPEM. It was seen, that thermal polymerization of side vinyl groups and thermal decomposition of the multimonomer appear within the 247—380°C range (under nitrogen). Introduction of 1 wt. % of AIBN under nitrogen reduces PPEM polymerization temperature to 136°C. PPEM undergoes photopolymerization at room temperature to crosslinked products.

Key words: poly[2-(4-pentenoyloxy)ethyl methacrylate], multimonomer, thermal polymerization, photopolymerization, photocrosslinking.

Multimonomers are interesting oligomers or polymers characterized by accumulated polymerizable double bonds along the main chain. Synthesis of two multimonomers — (meth)acrylic esters of oligomeric *p*-cresol-formaldehyde resin has been described for the first time by Kämmerer [1]. (Meth)acrylate groups in these multimonomers are combined by covalent bonds with a rigid skeleton of several *p*-cresol groups linked with methylene groups. Bamford [2] described a multimethacrylate prepared from poly(vinyl alcohol) esterified with methacryloyl chloride, and a similar system has also been examined by us [3]. Another type of multifunctional monomers has been prepared by us by means of the esterification of poly(2-hydroxyethyl methacrylate) (PHEMA) with (meth)acryloyl chloride [4]. Schotten-Bauman's esterification has turned out to be particularly suitable for the preparation of such polymeric multimonomers. A macromolecular multiallyl monomer has been synthesized by reacting poly(methacryloyl chloride) with allylamine in tetrahydrofuran [5]. Based on the obtained results during the examination of free-radical polymerization of these multimethacrylates, it has been found that linear ladder, branched or crosslinked polymers are formed depending on the process conditions.

The aim of the present study was to prepare a new type of multimonomer — the poly[2-(4-pentenoyloxy)ethyl methacrylate] (PPEM) — by reacting PHEMA with 4-pentenoyl chloride (4-PC); the reaction should proceed according to equation 1.



(1)

The intention was also to characterize the physical and chemical properties of the obtained PPEM.

EXPERIMENTAL

Materials

— 2-Hydroxyethyl methacrylate (HEMA) was purified by distillation under reduced pressure and the bp 87—89°C/5 mmHg fraction was collected.

— 4-Pentenoyl chloride, a commercial product of Fluka AG, was used without further purification.

— Tetrahydrofuran (THF) was refluxed over CaH_2 and, next, distilled and kept over molecular sieves 4 Å.

Preparation of PHEMA

Poly(2-hydroxyethyl methacrylate) (PHEMA) was prepared by radical polymerization of a 10% monomer solution in isopropanol. Concentration of the initiator (AIBN) was 20 wt. % relative to HEMA. Reaction temperature was 70°C, time was 5.5 h. The polymer was precipitated with a benzene-heptane mixture (v/v = 1:1), washed with acetone, and dried under reduced pressure at 50°C. Yield of 69% was attained. Number average molecular weight of PHEMA was M_n = 23 600 g/mol, (DP_n = 181) and polydispersity — M_w/M_n = 1.93.

Synthesis of PPEM

PPEM was prepared by Schotten-Bauman's esterification of PHEMA with 4-PC. The following optimum process parameters were found experimentally:

Solution A

Solution of PHEMA (H_2O:THF, v/v = 3:2), 0.5 mol/L groups OH	1 vol.
Aqueous solution of KOH, 3.0 mol/L	1 vol.
THF	1 vol.

Solution B

4-Pentenoyl chloride	1.2 mole-equiv. (to the hydroxyl groups in PHEMA)
THF	1.1 vol.
Toluene	0.2 vol.

Solution A was introduced into a three-necked flask provided with a stirrer and a thermometer, cooled down to -8°C and, next, solution B was added dropwise. The process was carried out with intensive stirring for 30 min and the resulting mixture was left for separation. The upper organic layer was separated from the lower one, in which only PHEMA esterified to a low degree remained. Next, the organic layer was dried over anhydrous $MgSO_4$. The product was precipitated with water and purified by dissolving in THF and reprecipitating with water. It was dried under reduced pressure at 40°C. The obtained PPEM contained 99.5 mole % of pendant 4-pentenoate groups, and constituted a viscous polymer with M_n = 28 300 g/mol. Analysis for $C_{11}H_{16}O_4$ (212.24) — calculated: C 62.25%; H 7.60%, — found: C 61.95%; H 7.49%.

The multimonomer prepared was easily soluble in solvents such as chloroform, acetone, THF, toluene, DMF and DMSO but was insoluble in water and heptane.

Photopolymerization of PPEM

A thin layer of PPEM was applied onto a KBr pellets by evaporation of solvent from the PPEM in chloroform and dried at a room temperature under vacuum. The resulting layer was irradiated with a L6/58 quartz tube (37.5 W) without filter kept at a distance of 20 cm. IR spectra were recorded on spectrophotometer after each irradiation stage. Percentage conversion of the double bonds in PPEM was calculated from the following formula:

$$\%conversion = \left(\frac{A_0 - A_t}{A_0}\right)\cdot 100\% \qquad (2)$$

where: *A_0 and A_t are the areas of* CH_2=CH- *bands at 1638 cm^{-1} before and after various irradiation times, respectively.*

Measurements

— Infrared spectra were obtained from thin films on KBr pellets using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) spectrophotometer.

— ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker DPX 250 MHz spectrometer with $CDCl_3$ as solvents and TMS as an internal reference.

— Product esterification degree was determined from elemental analysis for carbon and hydrogen.

— Values of number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w/M_n) of PHEMA were determined by gel permeation chromatography (GPC). Chromatogram in DMF at 35°C was obtained in Waters modular system using Ultrastyragel Linear Column and RI-detector Waters 410. Average molecular weight was calculated on the basis of a polystyrene calibration curve. The number average molecular weight of PPEM was determined by the use of Knauer membrane osmometer in toluene.

— Differential scanning calorimetry (DSC) was performed using Perkin Elmer, DSC-7 instrument with a heating rate of 20°C · min^{-1} from 40 to 380°C in a nitrogen atmosphere. Samples were obtained by dissolving of PPEM or PPEM and AIBN (1wt. %) in chloroform. Next, the solvent was removed under reduced pressure at room temperature. Approximately 10 mg samples were weighed accurately in aluminium DSC sample pan.

— Thermogravimetric (TG) analysis was performed using a TG-209 thermobalance (Netzsch), with measurments was carried out under a nitrogen atmosphere. A *ca.* 5 mg sample was used, at heating rate of 10°C · min^{-1} within the temperature range from 25 to 500°C.

RESULTS AND DISCUSSION

Spectral Characterization of PPEM

Figure 1 shows of FTIR spectra of PPEM (Fig. 1a) as well as of the initial PHEMA (Fig. 1b). PPEM exhibits an absorption band additional, to the initial PHEMA, at 3070 cm^{-1} (=CH_2), 1638 cm^{-1} (C=C), and 907 cm^{-1} (=CH-). However, the band at 3630—3050 cm^{-1} (OH) disappears.

^{1}H NMR spectrum of PPEM (Fig. 2a), shows signals of CH_2=CH- protons at δ = 5.04 ppm and δ = 5.83 ppm, -OCH_2CH_2O- protons at δ = 3.92—4.53 ppm, -CH_2CH_2- protons of the side chain at δ = 2.45 ppm, -CH_2- protons of the main chain at δ = 1.52—2.25 ppm and -CH_3 at δ = 0.65—1.45 ppm.

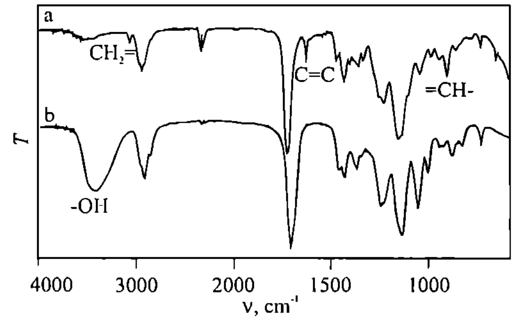


Fig. 1. FTIR spectra of: (a) — PPEM, (b) — PHEMA

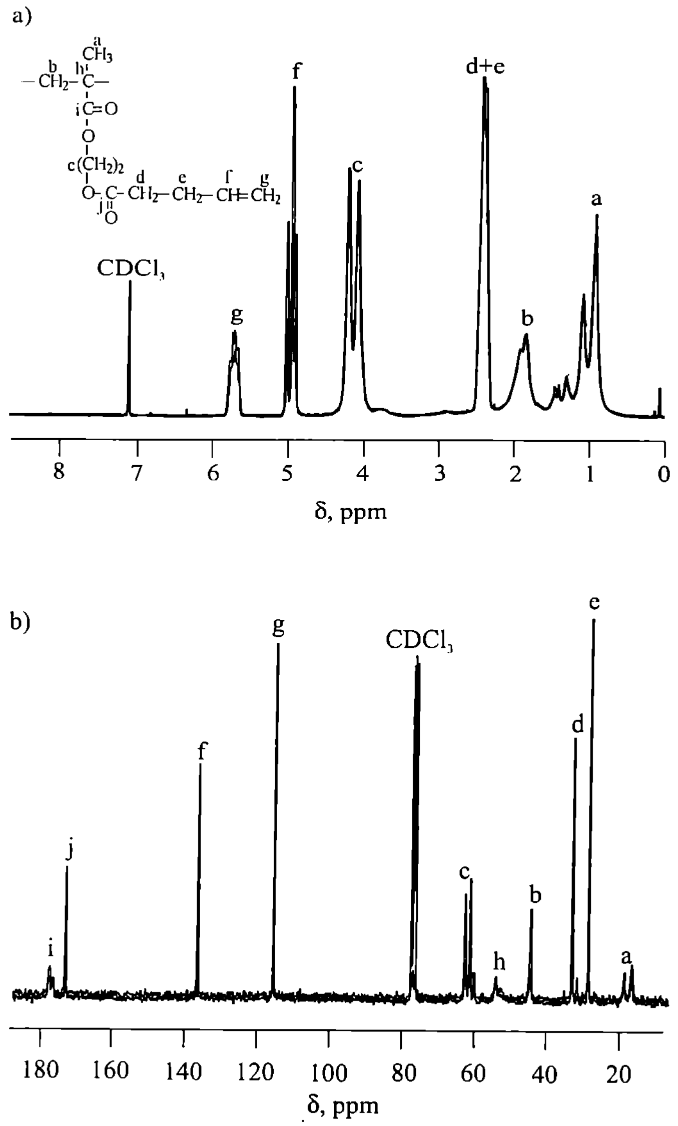


Fig. 2. PPEM spectra: (a) — ^1H NMR, (b) — ^{13}C NMR

Similar to ^1H NMR, the structure of PPEM was confirmed by taking a ^{13}C NMR spectrum and observing different types of resonance peaks for various carbon atoms (Fig. 2b). For instance, two well-separated resonance peaks appeared for carbon atoms of two carbonyl groups of similar type at δ = 172.46 and δ = 176.84 ppm, as well as resonance peaks for double bond carbons at δ = 115.47 and δ = 136.38 ppm.

FTIR, ^1H NMR and ^{13}C NMR spectra and results of elemental analysis confirm chemical structure of the obtained PPEM.

DSC studies of PPEM

Figure 3 shows DSC thermograms of PPEM itself and PPEM containing 1 wt. % of AIBN. The DSC thermogram of PPEM (Fig. 3a) exhibits a broad exothermic peak in the 247—380°C range under nitrogen. It probably results from the thermally initiated polymerization of vinyl double bonds, with thermal decomposition of PPEM occurring at the same time. This assumption is confirmed by analysis of the PPEM TG curve (Fig. 4) showing a visible loss of weight already at a temperature of about 265°C.

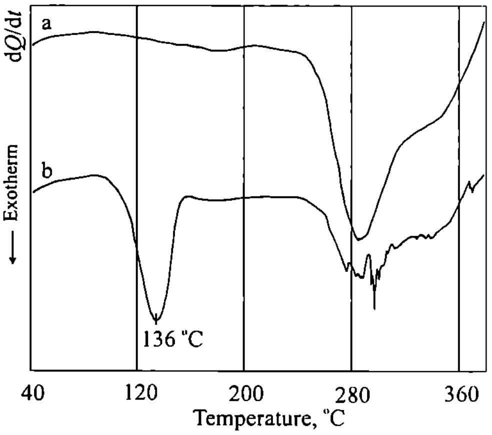


Fig. 3. DSC thermograms of: (a) — PPEM under inert atmosphere, (b) — PPEM with 1 wt. % AIBN under inert atmosphere

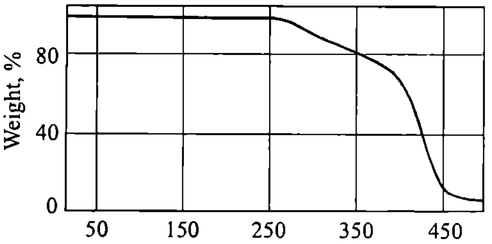


Fig. 4. TG curve of PPEM under inert atmosphere

Thermogram of PPEM containing 1 wt. % of AIBN (Fig. 3b) under nitrogen exhibits two exothermic peaks — a narrow one with minimum at 136°C and second a broad irregular peak in the 247—380°C range. The first peak is probably associated with the crosslinking polymerization of some double bonds initiated by radicals derived from AIBN decomposition. This is confirmed by the partial disappearance of the absorption band of $CH_2=CH$- in the sample spectrum (ν = 1638 cm^{-1}) after its heating up to 155°C and by the loss of its solubility in organic solvents. The second exothermic peak results, as in the case of PPEM itself, from thermally initiated polymerization of remaining vinyl groups, with endothermic decomposition of the sample occurring at the same time. Reina *et al.* [6] had obtained similar results for epichlorohydrin/ethylene oxide copolymer with pendant 4-pentenoate groups during the examination of their crosslinking by double bonds.

Photopolymerization of PPEM

Preliminary observations showed that PPEM is susceptible to the action of UV radiation. No change in absorption intensity of carbonyl group is observed after irradiation, but such intensity of unsaturated double bonds is considerably lower. This is probably due to double bonds breakage by UV radiation and subsequent crosslinking of the polymer, which becomes insoluble in the solvents. The course of this process is illustrated in Fig. 5. Thus, presence of double bonds capable of photopolymerization in PPEM makes it possible to use this multimonomer as a crosslinking agent in the preparation of networks. This issue will be studied further.

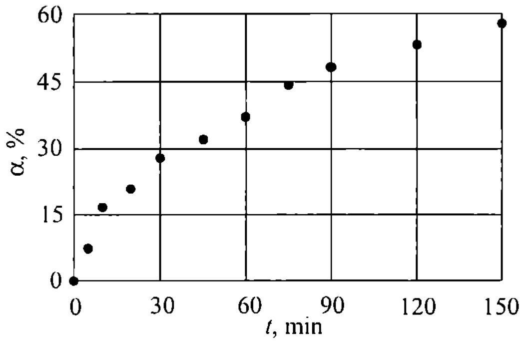


Fig. 5. Effect of irradiation time (t) on the conversion (α) of double bonds during the photopolymerization of PPEM

CONCLUSIONS

The studies performed have shown that the esterification of PHEMA with 4-PC by Schotten-Bauman's method results in a new multimonomer — *i.e.* PPEM. DSC data show that the use of a radical initiator causes PPEM to crosslink in a much lower temperature range as compared with temperatures of its thermal decomposition. Photopolymerization of PPEM in solid state results in formation of a crosslinked product.

ACKNOWLEDGMENTS

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