

Synthesis and characterization of poly[2-(10-undecenoyloxy)ethyl methacrylate]

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Summary

By Schotten-Baumann's esterification of poly(2-hydroxyethyl methacrylate) with 10-undecenoyl chloride a new multimonomer - poly[2-(10-undecenoyloxy)ethyl methacrylate] was prepared. Based on the results of elemental analysis, FTIR, ^1H -NMR and ^{13}C -NMR spectra, the structure of the multimonomer was proposed. The thermal properties of the multimonomer were studied by DSC and TG. The rate of disappearance of double bonds in the multimonomer during UV irradiation was examined in the solid state to obtain a crosslinked product.

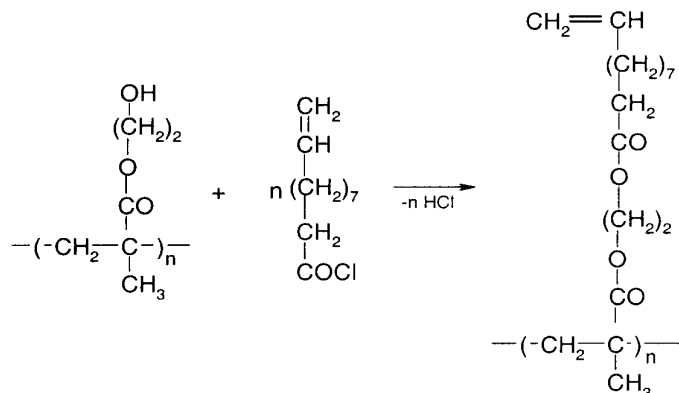
Introduction

The synthesis of two multimonomers – methacrylic and acrylic esters of oligomeric p-cresolformaldehyde resin has been described for the first time by Kämmerer [1]. In these multimonomers, (meth)acrylate groups are combined by covalent bonds with a rigid skeleton of several p-cresol groups linked with methylene groups. Bamford [2] described the 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) with acryloyl or methacryloyl chloride [4]. Schotten-Baumann's interfacial esterification has turned out to be particularly suitable for the preparation of these 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. Recently, Gimenez *et al.* [6] obtained 10-undecenoate esters of poly(vinyl alcohol) with different degrees of esterification which were studied in order to find how the concentration of reactive double bonds can influence the crosslinking process.

The aim of the present paper was to prepare a new multimonomer - poly[2-(10-undecenoyloxy)ethyl methacrylate] by reacting poly(2-hydroxyethyl methacrylate)

with 10-undecenoyl chloride according to the following Scheme I, as well as the physical and chemical characterization of the esterification product.



Scheme I

Experimental

Materials

2-Hydroxyethyl methacrylate (HEMA) was previously purified by distillation under vacuum. 10-undecenoyl chloride was a commercial product of Fluka. Tetrahydrofuran (THF) was refluxed over CaH_2 and then distilled and kept over molecular sieves (4 Å). Poly(2-hydroxyethyl methacrylate) (PHEMA) was prepared by polymerization of a 10% solution of monomer in isopropanol. The concentration of AIBN was 20% by wt. in relation to HEMA. The reaction temperature was 70 °C, time 5.5 h. The polymer was precipitated with benzene-heptane mixture 1:1 by vol., washed with acetone, and dried under vacuum at a temperature of 50 °C. Molecular weight of PHEMA was $M_n = 16.700$ g/mol. Yield 69%.

Synthesis of poly[2-(10-undecenoyloxy)ethyl methacrylate] (PUDEM)

PUDEM was prepared by Schotten-Baumann's interfacial esterification of PHEMA with 10-undecenoyl chloride. The optimum process parameters were found experimentally:

Solution A

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

Solution B

10-undecenoyl chloride	1.3 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 equipped with a stirrer and a thermometer, cooled down to -8 °C, and then solution B was added dropwise. The reaction was carried out with intensive stirring for 80 min, and then the mixture was left for separation. The upper organic layer was separated from the lower one, in which remained only the PHEMA esterified to a low extent. Next, the organic layer was dried with anhydrous MgSO_4 . The product of esterification was precipitated with water and purified by dissolving in THF and reprecipitating with water. It was dried

under reduced pressure at 50 °C. The obtained PUDEM contained 99.4 mole% of pendant 10-undecenate groups, showing an appearance of a viscous polymer with $M_n = 27.500$ g/mol. Yield 86%. $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.85$, 1.05 (d,3H, CH_3), 1.30 (s,10H, $(\text{CH}_2)_5$), 1.62 (s,2H, CH_2), 1.84 (s,2H, CH_2), 1.92 (s,2H, CH_2), 2.05 (s,2H, CH_2), 4.15, 4.26 (d,4H, $(\text{CH}_2)_2$), 4.95 (t,2H, $\text{CH}_2=$), 5.82 (s,1H, $=\text{CH-}$). $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 15.99$, 17.84 (CH_2), 23.68, 27.94, 28.15 (CH_2), 32.83 (CH_2CO), 43.80 (CH_2), 53.29 (C), 60.31, 61.78 ($-\text{OCH}_2\text{CH}_2\text{O-}$), 113.37 ($\text{CH}_2=$), 138.10 ($=\text{CH-}$), 172.43, 175.95 (C=O). FTIR (cm^{-1}): 3070 ($\text{CH}_2=$), 1730 (C=O); 1638 (C=C), 907 ($=\text{CH-}$). Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4$ (296.41): C, 68.88%; H, 9.52%, Found: C, 68.44 %; H, 9.21%.

Photopolymerization

A thin layer of PUDEM was applied onto a KBr plate by the evaporation of the solvent from the chloroform solution and then dried at room temperature under a vacuum. The layer obtained was irradiated with a L6/58 quartz tube (37.5 W) without filter from a distance of 20 cm at room temperature. The rate of disappearance of the absorbance of $\text{CH}_2=\text{CH-}$ ($\nu = 1638 \text{ cm}^{-1}$) in PUDEM after various irradiation times was estimated using an FTIR spectrophotometer.

Preparation of samples PUDEM for performing DSC

Samples were obtained by dissolving of PUDEM or PUDEM and AIBN (1% w/w) in chloroform. Then, the solvent was removed under reduced pressure at room temperature. Approximately 10 mg samples were weighed accurately in aluminium DSC sample pan.

Measurements

Infrared spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained using a Bruker DPX 250 MHz spectrometer with CDCl_3 as solvent and TMS as an internal reference. The degree of the esterification was determined from the carbon and hydrogen content of the product, as measured by elemental analysis. Differential scanning calorimetry (DSC) was performed using Perkin Elmer, DSC-7 instrument with a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ from 50 to $400 \text{ }^\circ\text{C}$ in a nitrogen atmosphere. The sample of about 10 mg was placed in an aluminum pan sealed by an aluminium cover. The thermogravimetric (TG) investigations were performed using a thermobalance TG-209 of Netzsch, measurements were carried out in a nitrogen atmosphere (sample of about 5 mg, a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ within the temperature range from 25 to $500 \text{ }^\circ\text{C}$). The number-average molecular weights of PHEMA and PUDEM were determined in isopropanol and toluene as solvents, respectively, by use of a Knauer membrane osmometer.

Results and discussion

Spectral characterization of PUDEM

The hydroxyl groups of the PHEMA were esterified by introducing crosslinkable 10-undecenate pendant groups. The chemical structure of the polymeric multimonomer was determined by means of FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy as well as

elemental analysis.

In the FTIR spectrum of the esterification product (not shown), additional absorption bands, as compared with the initial PHEMA, appear at 3070 cm^{-1} ($\text{CH}_2=$), 1638 cm^{-1} ($\text{C}=\text{C}$) and 907 cm^{-1} ($=\text{CH}-$). On the other hand, there disappears the band in the range $3630 - 3050\text{ cm}^{-1}$ derived from the hydroxyl groups of PHEMA.

The $^1\text{H-NMR}$ spectrum of PUDEM (Figure 1) shows the following chemical shifts of protons: for $\text{CH}_2=\text{CH}-$ at 4.94 ppm and 5.82 ppm , for $-\text{O}(\text{CH}_2)_2\text{O}-$ at $4.02\div 4.48\text{ ppm}$.

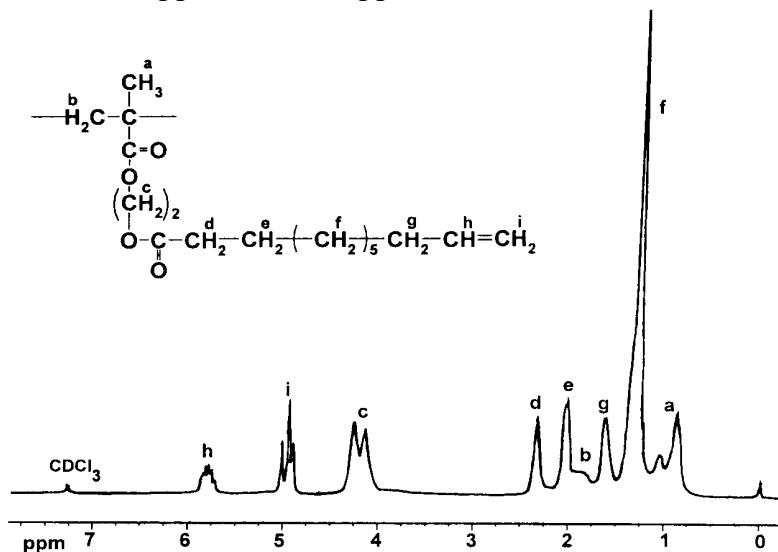


Figure 1. $^1\text{H-NMR}$ spectrum of PUDEM

Other signals corresponding to the aliphatic protons of the side chain appear between $1.08 - 2.48\text{ ppm}$.

Similar to $^1\text{H-NMR}$, the structure of PUDEM was confirmed by $^{13}\text{C-NMR}$ spectrum where different types of resonance peaks were observed for various carbon atoms (Figure 2). For instance, two well-separated resonance peaks were obtained for carbon atoms of two carbonyl groups of similar type at 172.43 and 175.95 ppm as well as resonance peaks for double bond carbons at 113.37 and 138.10 ppm .

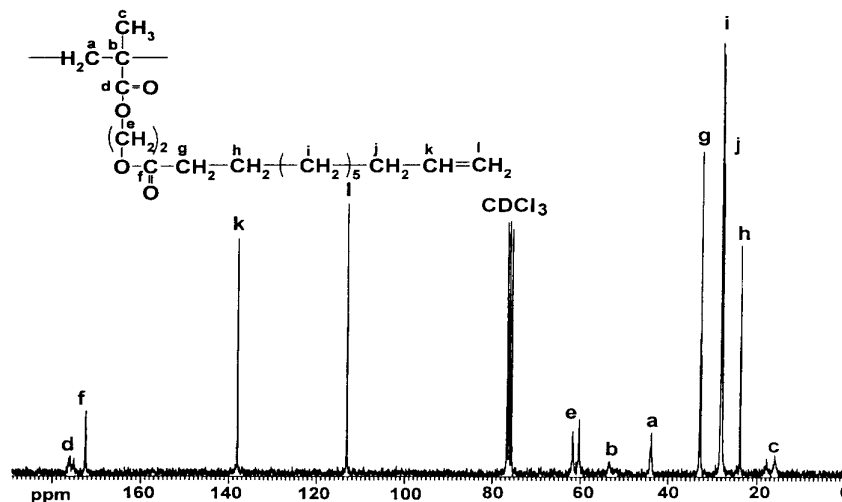


Figure 2. $^{13}\text{C-NMR}$ spectrum of PUDEM

The FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra and the results of elemental analysis confirm the chemical structure of the obtained 10-undecenoate ester of PHEMA.

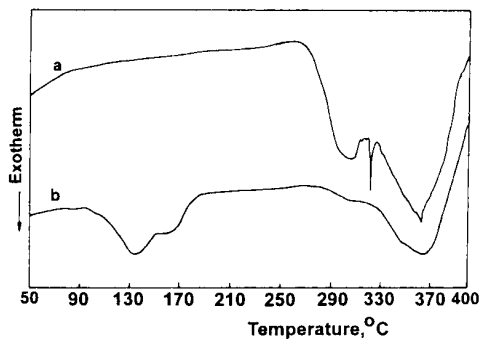


Figure 3. DSC thermograms of (a) PUDEM, (b) PUDEM with 1% by wt AIBN, in inert atmosphere

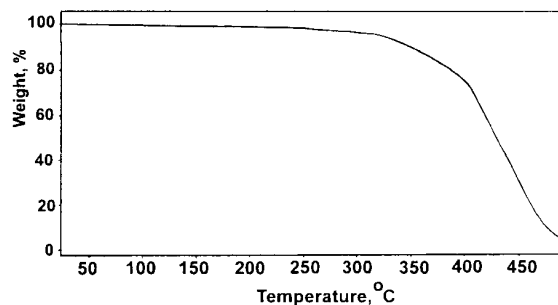


Figure 4. TG curve of PUDEM, in inert atmosphere

Thermal studies of PUDEM

Figure 3 shows DSC thermograms of PUDEM itself (curve a) and PUDEM containing 1% by wt. of AIBN (curve b). The DSC thermogram of PUDEM (Figure 3a) shows a broad irregular exothermic peak in the range 265 – 400 °C under a nitrogen atmosphere. It probably results from the thermal crosslinking of vinyl double bonds, with the thermal decomposition of PUDEM occurring at the same time. This assumption is confirmed by the analysis of the TG curve of PUDEM (Figure 4) showing a visible loss of weight already at a temperature of 275 °C under a nitrogen atmosphere. In the case of PUDEM containing 1% by wt. of AIBN, its thermogram (Figure 3b) shows two broad exothermic peaks within the temperature ranges 88 – 186 °C and 272 – 400 °C. The first one is probably associated with the crosslinking polymerization of some double bonds initiated by the radicals derived from the initiator decomposition. This is confirmed by the partial disappearance of the absorption band of $\text{CH}_2=\text{CH}-$ in the spectrum ($\nu = 1638 \text{ cm}^{-1}$) of the sample after its heating up to 186 °C and the loss of its solubility in organic solvents. On the other hand, the second exothermic peak results from the thermally initiated polymerization of the remaining vinyl groups, with the endothermic decomposition of the sample occurring at the same time. This is consistent with the results obtained by Gimenez *et al.* [6] for 10-undecenoate esters of poly(vinyl alcohol) with different degrees of esterification.

Photopolymerization of PUDEM

Preliminary observation showed that PUDEM is susceptible to the action of UV radiation. Figure 5 shows a part of IR spectrum of PUDEM before and after 180 min UV irradiation. This fragment comprises the range where absorption bands related to $\text{CH}_2=\text{CH}-$ and $>\text{C}=\text{O}$ appear.

After irradiation of the sample under investigation, one can observe a broadening of the absorption band of the carbonyl group at 1730 cm^{-1} (the area of this band is approximately constant), while the intensity of the absorption band of $\text{CH}_2=\text{CH}-$ ($\nu = 1638 \text{ cm}^{-1}$) is decreased. This is probably due to cleavage of double bonds by UV

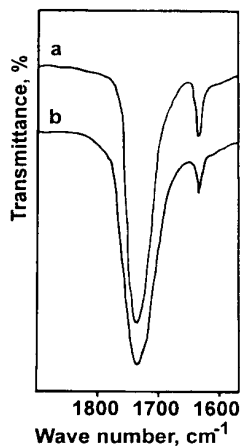


Figure 5. Section of the IR spectrum of PUDEM: (a) before irradiation, (b) after irradiation for 180 min

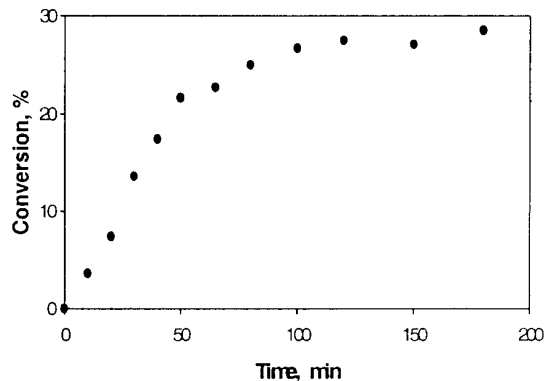


Figure 6. The conversion of $\text{CH}_2=\text{CH}-$ vs. irradiation time

radiation and the formation of crosslinkings in the polymer which results in a product insoluble in organic solvents. This process is illustrated in Figure 6 which shows the conversion of $\text{CH}_2=\text{CH}-$ vs. irradiation time. The presence of double bonds capable to photopolymerization in PUDEM makes it possible to use PUDEM as crosslinking agent in the preparation of networks. This issue will be subject of further studies.

Conclusions

The studies performed have shown that the esterification of PHEMA with 10-undecenoyl chloride by Schotten-Baumann's method results in a new multimonomer - poly[2-(10-undecenoyloxy)ethyl methacrylate] in which double bonds are combined with the main chain via the long spacer. From the DSC data it follows that the use of the radical initiator causes PUDEM to crosslink with a lower temperature range than that of its thermal decomposition. The photopolymerization of PUDEM in the solid state results in a crosslinked product.

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