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1 Initiation of polymerization of pure
2 2-hydroxyethylmethacrylate under shock
3 wave compression

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16 **Key words:** radical polymerization, shock wave compression, HEMA, oligomers

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21 **Abstract**

22 The ability to initiate chemical reactions without needs of potentially hazardous solvents,
23 catalysts and radical initiators is of key importance for modern biotechnologies and medicine.
24 In this study, laser-driven shock wave compression was performed on pure
25 2-hydroxyethylmethacrylate (*HEMA*) free of any additives in order to trig the polymerization
26 process. We showed that the generated peak shock-wave pressure in the range between 2 and
27 5.5 Gpa permitted initiation of radical polymerization and formation of poly-*HEMA*
28 oligomers. The reaction begin with diradicals $HEMA_2^{\bullet\bullet}$ appeared at the peak pressure and, by
29 reactions with *HEMA* monomers, forming $HEMA_3^{\bullet\bullet}$ diradicals on the 20-ns timescale. The
30 chain propagation further occurs on the sub- μ s timescale by associations of the trimer
31 diradicals, which, because of a smaller reactivity, do not react with *HEMA* monomers. The
32 proposed method can be considered for scale-up of polymerization process of ultrapure
33 organics.

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36 **1. Introduction**

37 High pressures (HP) processing is an effective way to realization of ultrapure polymers via
38 radical activations, otherwise requiring addition of thermo- or photo- initiators to a monomer
39 solution. One of the most significant advantages of HP chemistry is the ability to initiate
40 chemical reactions without the need of potentially hazardous solvents, catalysts, or radical
41 initiators [1-3]. In the past, the HP polymerization of small, unsaturated hydrocarbon
42 molecules in liquid and crystalline phases has been extensively studied both experimentally
43 and theoretically [4, 5]. However, due to the reduction of molecular mobility with increasing
44 pressure, this approach is restricted to monomers in ordered phases, in which the
45 polymerization does not require large molecular rearrangements. Pure polymer and
46 polymer-based materials may have a great potentiality for applications in biomedicine,
47 photonics, etc. In the same time, any practical large-scale implementation of this method and
48 materials is limited by a very small reaction volumes characteristic of GPa high-pressure cells.
49 The research on scale-up of the HP-polymerization process is therefore of high actuality.

50 To produce and apply high pressure on a given substance in order to induce a chemical
51 reaction, there are two main approaches: static and dynamic. For the generation of high static
52 pressure, the application of a mechanical force to the surface of the sample that is placed in a
53 vessel such as diamond anvil cells (DAC). Generally, the DAC allows a pressure limit above
54 10 GPa and to combine with probing techniques for performing in situ observations of
55 materials [6-8] . Shock wave compression created by gas cannons, pulsed lasers, high pulsed
56 electrical currents, and explosions is the basis for dynamic techniques. Today, it is possible to
57 generate pressures up to 5 GPa and even higher in the condensed matter [9]. In such extreme

58 conditions, atomic bonding and electronic structure of species significantly changed at the
59 ns- μ s timescale compared to that in ambient conditions, creating opportunity for the
60 activation of chemical transformations. The application of the dynamic HP processing to
61 organic polymerization can be of interest. The main issue in this respect concerns the process
62 kinetics, which remains largely unknown.

63 The poly-2-hydroxyethyl methacrylate (pHEMA) is a biocompatible material, which is
64 considered in biomedicine for fabrication of artificial cornea, contact lenses, etc. [10-13]. It
65 can be photopolymerized in ambient conditions using a photoinitiator [14] or without catalyst
66 under moderate HP (< 1GPa) [15]. Recently, an important improvement of the HP
67 polymerization process of 2-hydroxyethylmethacrylate (HEMA) has been developed in our
68 institution [16], which was realized in a HP DAC cell by applying two-stage static HP
69 processing. An effective polymerization has been achieved also in HEMA-based
70 organic-inorganic hybrid materials using this method with unprecedentedly high monomer
71 conversion yield, well above that obtained via conventional methods using thermal and photo
72 initiators [17] at the same concentration of the inorganic component. In this work, we applied
73 a laser driven shock-wave compression to investigate the possibility of initiation of bulk
74 HEMA polymerization.

75

76 **2. Materials and Methods**

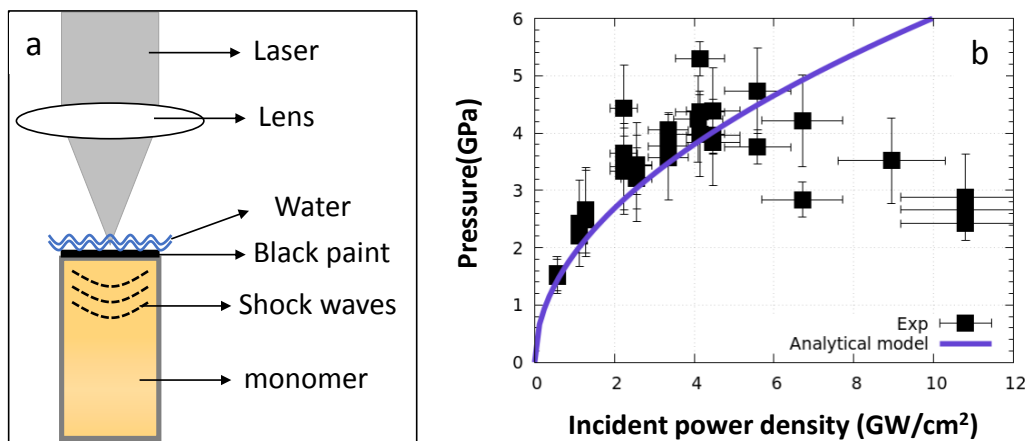
77 *2.1. Chemicals*

78 The monomer was supplied by Sigma Aldrich (St. Louis, MO, USA) and provided in the
79 liquid form with the following reference: 2-hydroxyethyl methacrylate (HEMA), CAS:

80 868-77-9, $\geq 99\%$.

81 2.2. Laser-driven shock wave compression

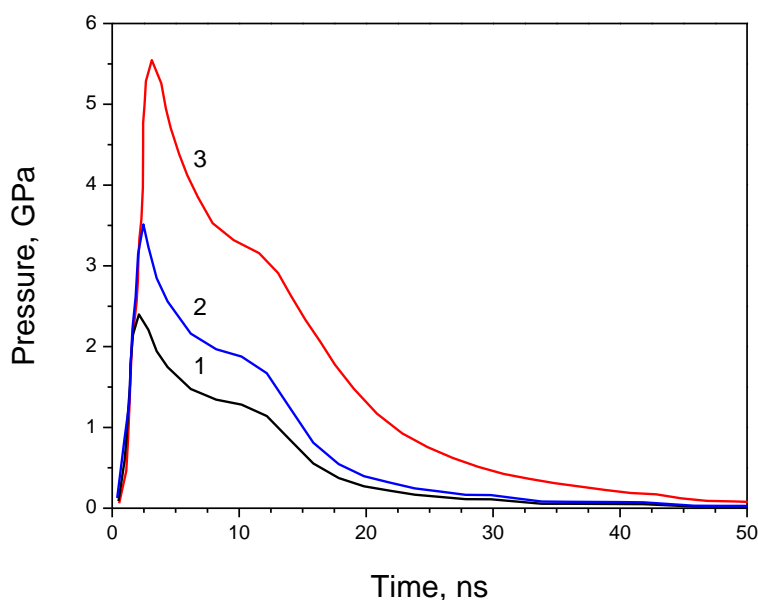
82 The schema of the laser-driven shock compression (LSC) experiment depicted in Fig. 1a
83 has been described in details in Ref. [18]. In short, LSC was obtained after receiving laser
84 pulses provided by BIVOJ laser system of HiLase with energy E between 0.5 and 7 J
85 ($\lambda=1030$ nm, pulse duration $\tau\sim 10$ ns) on a target with the square spot area of $\sigma=1.94\times 1.94$
86 mm^2 . In multiple LSC experiments, laser shots have a repetition rate of 0.5 Hz. The HEMA
87 samples were placed in black-painted aluminum cells and mounted on a holder of robot Fanuc
88 M-20iA/20M (load of up to 20 kg with 0.08 mm positioning repeatability). Water was used as
89 a confining medium. In order to ensure stable and reliable treatment, the laser energy and
90 beam shape were monitored by a diagnostic system based on two cameras (MANTA G-125,
91 Allied Vision) and a calibrated photodiode. The shock wave pressures $2\leq P_{\text{max}}\leq 6$ GPa
92 obtained in the experiments are shown in Fig. 1b as a function of laser power density ($E/\tau\sigma$).
93



94
95 *Figure 1. Schematic configuration of laser shock peening (a) and correlation between laser incident*
96 *power density and generated pressure (b).*

97 The measured pressure kinetics is shown in Fig. 2. It includes a rather sharp peak P_{max}

105
104 followed by a longer tail of the pressure decrease down to ~ 0.1 GPa level. The absolute
103 values depend on the applied laser energy in a pulse. For example, in case of the maximum
102 energy 2.5 J/pulse used in present experiments, the peak pressure of $P_{\max}=5.5$ was attained
101 with the full width at half maximum of $t_{1/2}\approx 15$ ns and relaxation time below 0.1 GPa pressure
100 of $t_r=50$ ns. These results are in agreement with previous experiments and modelling of the
99 water-confined regime [9]. The pressure kinetics will be useful for understanding of the
98 relevant reaction rates.

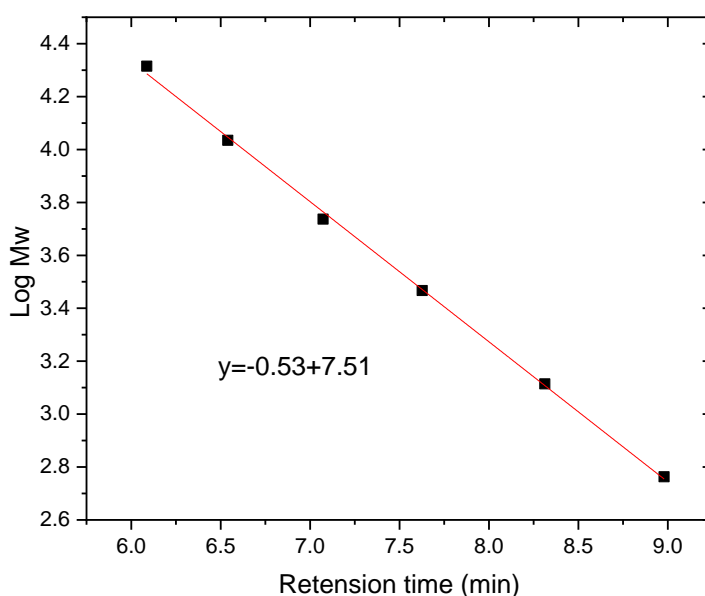


106
107 *Figure 2. Pressure dependence in LSC experiments at laser pulse energy of 0.5 J (1), 1 J (2) and 2.5 J*
108 *(3).*

109 2.3.Characterization

110 The molecular weight and polydispersity of the polymeric chains have been evaluated
111 using gel penetration chromatography (GPC). After been exposed to LSC, the closed cells
112 with HEMA solutions were kept in a glove box under inert gas atmosphere until GPC
113 analysis. For sample preparation, 50 μL of the monomer liquid treated by LSC process was

114 mixed with 400 μ L tetrahydrofuran (THF) in order to dissolve the possible solid polymer.
115 Dionex Ultimate 3000 GPC apparatus was equipped with a Polymer Laboratories MesoPore
116 3- μ m column (300x7.5 mm) in an isothermal oven (35 $^{\circ}$ C) in series with a UV-visible
117 detector (detection wavelength 210 nm). The eluent flow rate (HPLC grade tetrahydrofuran,
118 THF) was set to 1.0 mL/min. A particular attention was paid to the calibration of column for
119 low molecular weights 100-1000 g/mol. The calibration, shown in Fig. 3, was performed
120 using a set of polystyrene standards (EasiCal PS-2 Polymer Laboratories,
121 Mw = 580–20650 g/mol range) with a very narrow polydispersity, including ethylene glycol
122 dimethacrylate (CAS: 97-90-5, molecular weight 198.22 g/mol) and lauryl methacrylate
123 (CAS: 142-90-5, molecular weight 254.41 g/mol). Data acquisition and analysis were
124 performed with Chromeleon V 6.80 software supplied by Dionex.
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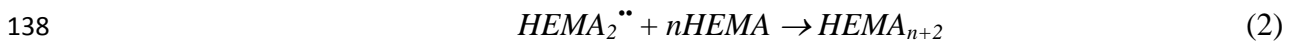
Figure 3. Calibration curve for gel penetration chromatography.

129 **3. Results and Discussions**

130 Under static HP, it has been previously shown [16] that the conversion yield of HEMA
131 monomers exhibits a threshold at P=2 GPa and reaches a plateau with a maximum of 90% at
132 pressures $P \geq 6.5$ GPa. This range of pressures was assigned to the formation of $HEMA_2^{\bullet\bullet}$
133 diradicals

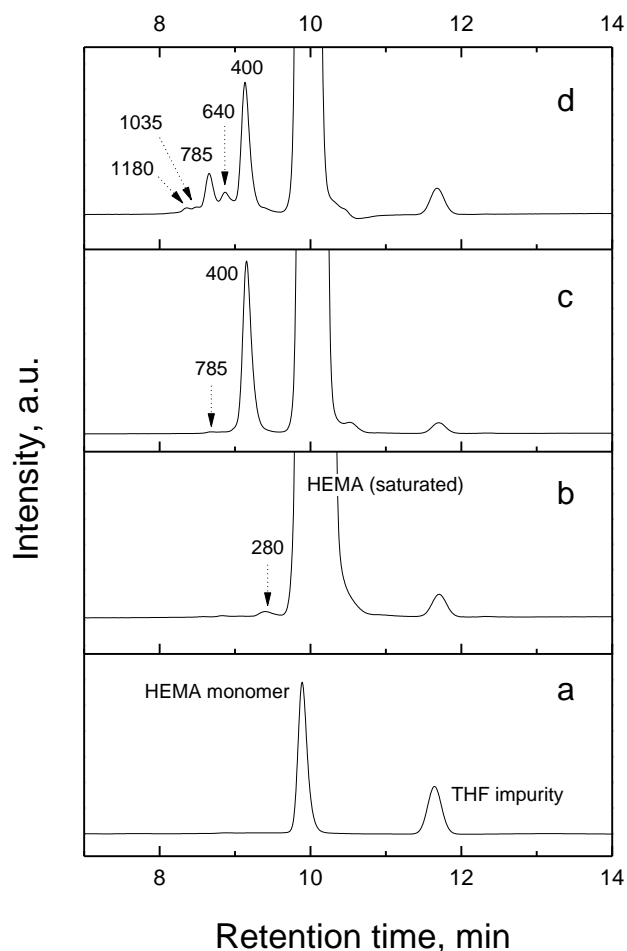


135 which activate the polymerization process on the second stage, when pressure is reduced
136 below 2 GPa, which fits the glass transition pressure, letting the monomers free to move
137 forming the polymer chains after the termination process:



139 In LSC process, the peak pressure was controlled via laser energy according to Fig. 1b.
140 The chromatograms of liquid pristine HEMA and HEMA samples after the exposition to LSC
141 with different laser energies are shown in Fig. 4. The THF impurities and HEMA monomer
142 (molecular weight 130 g/mol) were respectively detected at 11.64 and 9.89 min (Fig. 4a).
143 With low laser energy of 0.5 J providing the peak pressure of 2.2 GPa (close to the diradicals
144 activation threshold), a very weak GPC peak with the molecular weight of ~280 g/mol could
145 be seen, which corresponds to the molecular dimers $HEMA_2$. By increasing the laser energy
146 to 1 J (3.5 GPa), a peak of the larger chain with the molecular weight of 400 g/mol assigned
147 to $HEMA_3$ became intense and a new rather weak peak appeared with molecular weights of
148 785 g/mol (8.64 min), which was assigned to $HEMA_6$. With even higher laser energy of 2.5 J,
149 which correspond to the highest shock wave pressure of $P=5.5$ GPa, the peak of $HEMA_6$
150 intensified and three more peaks at 640 g/mol (strong), 1035 g/mol (weak) and 1180 g/mol

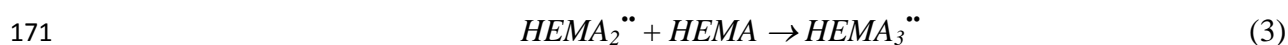
151 (weak) made their appearance, which were respectively assigned to HEMA₅, HEMA₈ and
 152 HEMA₉ chains. These observations allowed proposing the reaction scheme of the oligomers
 153 formation, which is discussed below.
 154



155
 156 *Figure 4. GPC patterns of pristine HEMA (a) and HEMA samples after LSC processing with one laser*
 157 *pulse of energy 0.5 J / P=2.2 GPa (b), 1 J / P=3.5 GPa (c) and 2.5 J / P=5.5 GPa (d). Molecular*
 158 *weights are indicated in g/mol units.*

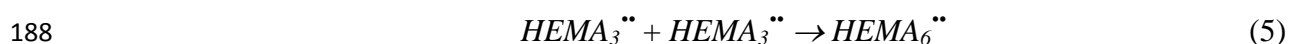
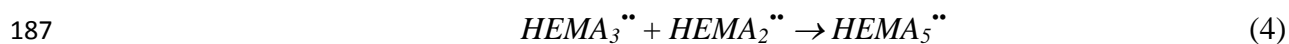
159 The Flory mechanism has been previously adopted for the self-initiation of polymerization
 160 in methacrylates (M) [19]. According to this mechanism, two monomers M combine to form
 161 a diradical $\cdot M_2$, which reacts with a third monomer molecule to generate two monoradicals

162 M_2^{\bullet} and M^{\bullet} able to initiate polymerization. In agreement with this mechanism and our
163 observations under static HP [16], we postulate that the diradical $HEMA_2^{\bullet\bullet}$ is readily formed
164 under high pressures above 2 GPa and initiates polymerization process when pressure is
165 released below 2 GPa, i.e. that of the glass transition. This $HEMA_2^{\bullet\bullet}$ diradical is formed
166 almost instantaneously (Eq. 1) via tail-to-tail addition of monomers occasionally having a
167 suitable alignment in the bulk glassy HEMA. By increasing LSC peak pressure, the yield of
168 the $HEMA_2^{\bullet\bullet}$ diradicals increased. The vanishing of the GPC peak corresponding to $HEMA_2$
169 dimers (Fig. 4c-d) supports our hypothesis of the very fast reaction kinetics of the dimer
170 diradicals with surrounding monomers, forming unsaturated trimers:

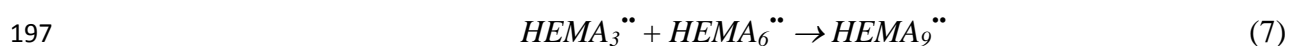
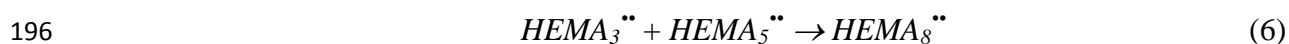


172 where the termination reaction $HEMA_3^{\bullet\bullet} \rightarrow HEMA_3$ probably occurs via intra molecular
173 processes as observed in the case of MMA self-polymerization at high temperatures ($>100^\circ\text{C}$)
174 [20]. Here we postulate the formation of the trimer diradicals $HEMA_3^{\bullet\bullet}$ because of their
175 preferential association in larger oligomeric chains, as it will be discussed below. Taking into
176 account the characteristic LSC pressure kinetics (Fig. 2) and relevant range of pressures
177 $0.1 < P < 2$ GPa enabling effective HEMA monomers conversion [16], one can conclude that
178 reaction (3) is completed within 50-ns time. Contrary to the mechanism proposed at ambient
179 pressure [21], it seems however that the steric hindrance induced by the HP environment
180 prevents the formation of monoradicals by transfer or abstraction of H from the diradical to a
181 third monomer. On the other hand, Fig. 4c shows that kinetics of formation of the larger
182 chains is slow and cannot be completed during the short time of ~ 100 ns. Obviously, the
183 appearance of large oligomers at $P=5.5$ GPa (Fig. 4d) is due to an increase of concentration of

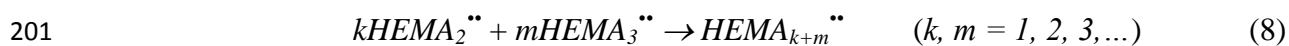
184 the activated species. Apparently, reactivity of the trimer diradicals is smaller compared to
 185 that of the dimer diradicals (3), prohibiting their fast association with monomers into HEMA₄.
 186 However, their association with other activated species can still be effective:



189 This conclusion is supported by our experimental observations of HEMA₅ (640 g/mol) and
 190 HEMA₆ (785 g/mol) oligomers in Fig. 4d. The smaller GPC peak of HEMA₅ compared to
 191 HEMA₆ is then explained by the strong *HEMA*₂^{••} diradicals consumption in process (3),
 192 which made the trimer diradicals more abundant in the solution. The same consideration may
 193 also explain a weak formation of tetramer HEMA₄ from two dimer diradicals. The
 194 subsequent reactions leading to HEMA₈ and HEMA₉ oligomers formation are due to the
 195 further associations of *HEMA*₃^{••} with species formed in processes (4) and (5):



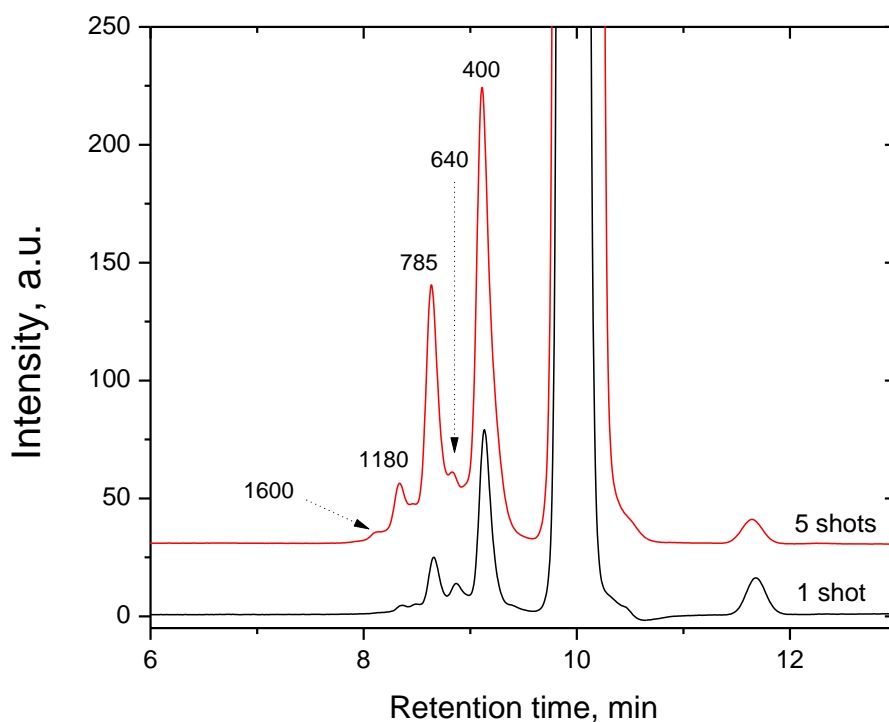
198 As a result of the appeared “magic numbers” n=2, 3, 5, 6, 8, 9 of HEMA_n oligomers in the
 199 initial polymerisation propagation, we propose a generalised schema of the HEMA chains
 200 growth at high pressures based on the diradicals association:



202 Furthermore, we ascribe diradical nature to these species, because of their selective
 203 association with *HEMA*₂^{••} and *HEMA*₃^{••} diradicals, despite of a low concentration in the
 204 reaction solution. As mentioned above, in all these reactions the terminations reaction may
 205 occurs via intra molecular processes. We notice that the GPC analysis used in the present

206 study do not allow us concluding about a specific termination mechanisms involved in the
207 formation of the observed oligomers. However, since the chains propagation takes place at
208 pressures below that of the glass transition, we conclude that a longer confinement time
209 ($t \gg 100$ ns) of the solution at moderate pressures of $0.1 < P < 2$ GPa would be required in order
210 to effectively complete the polymerization process. The effect of a longer exposure to these
211 relatively lower pressures could be seen in Fig. 5, where the GPC sample analysis after an
212 exposition to 1 and 5 laser pulses of 2.5-J energy is shown.

213



214

215 *Figure 5. GPC patterns of HEMA samples after LSC processing with 1 and 5 laser pulses of energy*
216 *2.5 J (peak pressure 5.5 GPa).*

217 In case of an additive process, the GPC patterns could not be expected to change much. In
218 contrast, relative intensities of the peaks at smaller times, which correspond to larger HEMA

219 chains were significantly intensified with an increase of the shock waves number. In
220 particular, while relative intensities of HEMA₃ and HEMA₅ remain the same, those of
221 HEMA₆ and HEMA₉ increased significantly. The last corresponds to the 5-times longer
222 reactions time of the trimer diradicals in processes (5) and (7). Furthermore, a shoulder
223 appeared at 8.15 min, which corresponds to chains with the molecular weight of 1600 g/mol.
224 According to Eq. 8, this corresponds to a successive association of four trimer diradicals
225 $HEMA_3^{**}$ ($m=4$), which last step is:



227 All these observations support the conclusion on the polymerisation propagation at moderate
228 pressures (below 2 GPa) in course of diradicals association. We notice in this connection that
229 the m -series of Eq. 8 involving $HEMA_3^{**}$ diradicals dominate the initial chains propagation
230 process. In contrast, the chains propagation by association of $HEMA_2^{**}$ diradicals is of lower
231 probability because of their rapid reaction (3) with the surrounding monomers, completed on
232 the sub- μ s timescale, giving rise to $HEMA_3^{**}$ diradicals.

233 The methacrylate diradical $\cdot M_2$ has been shown to be key compound in the initiation
234 mechanism of the spontaneous polymerization of methyl methacrylate [22]. However, even at
235 high temperature the reaction is extremely slow and showed a low conversion of monomer to
236 polymers. On the other hand, in methyl methacrylate an efficient conversion of monomers to
237 oligomers such as unsaturated dimers and trimers or 1,1,2,2-tetrasubstituted cyclobutanes has
238 been observed [20, 23-25] These earlier studies have suggested that diradicals cannot grow
239 into two directions, and they have to be terminated first on one side by a transfer reaction in
240 order to yield high polymers. The low polymerization yield is then the result of a competition

241 with the efficient self-termination processes of dimers and trimers diradicals. The
242 spontaneous polymerization therefore propagates at ambient conditions via transfer agents
243 forming polymerizable monoradicals. Our results clearly indicate that that the reactivity is
244 affected by high pressures where the polymerization propagates through the oligomer
245 diradicals association towards much larger polymeric species.

246 Because of a large affected volume compared to common high-pressure cells and
247 attainable 5 GPa pressures required for an effective radicals activation, LSC can be
248 considered for the scale-up of HPR polymerization process [16]. Unfortunately, the short
249 shock wave exposure time to the relevant moderate pressures of $\leq 0.1 \mu\text{s}$ is not sufficient to
250 accommodate the chains propagation kinetics and, consequently, it does not allow effectively
251 completing the polymerization process. However, the required pressure of the sub-GPa range
252 is not restrictive and could be achieved in large volumes using conventional available
253 techniques [26]. Therefore, combining shock-wave compression with post-exposure to
254 moderate static pressures could be main steps of a large-scale process for ultrapure polymers
255 production.

256

257 **4. Conclusions**

258 We report on initiation of the 2-hydroxyethylmethacrylate (HEMA) polymerization
259 process via laser-driven shock-wave compression. The gel penetration chromatography (GPC)
260 analysis of the chains mass was performed after the bulk monomer solution exposure to
261 different laser energies and number of pulses. We showed that generated pressure in the range
262 between 2 and 5.5 Gpa permitted initiation of the radical polymerization with the formation

263 of oligomers $HEMA_n$ (up to $n=12$). We confirmed the process initiation with $HEMA_2^{\bullet\bullet}$
264 diradicals and showed that they rapidly react on the 15 ns timescale with HEMA monomers
265 forming $HEMA_3^{\bullet\bullet}$ diradicals. The subsequent dominant chain propagation by association of
266 $HEMA_3^{\bullet\bullet}$ diradicals was evidenced. The shock-wave compression can be considered for the
267 scale-up of ultrapure organic polymerization process.

268

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276 15_006/0000674-01 HiLASE Centre of Excellence.

277

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