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poly(isobornylacrylate-co-isobutylacrylate)**

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1 **Effect of structure on the glass transition temperatures of linear and crosslinked**  
2 **poly(isobornylacrylate-co-isobutylacrylate)**

3  
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23

24 **Abstract**

25 A series of linear acrylic copolymers based on Isobornyl acrylate (IBOA) and isobutyl  
26 acrylate (IsoBA) were elaborated by radical photopolymerization. In addition, several  
27 photochemically crosslinked poly(IBOA-co-IsoBA) were prepared by introducing small  
28 amounts of 1,6-hexanedioldiacrylate as crosslinking agent. The evolution of the glass  
29 transition temperature was determined experimentally by Differential Scanning Calorimetry  
30 as a function of composition for both linear and crosslinked poly(IBOA-co-IsoBA), yielding  
31  $T_g$  values ranging from ( $\sim 249\text{K}$ ) to ( $\sim 315\text{K}$ ). Theoretical modeling was performed applying  
32 Fox, Gordon-Taylor and Couchman-Karasz models by simple calculations using experimental  
33 data, leading to only fair agreement between theoretical and experimental values, or by  
34 applying fitting procedures involving one or two adjustable parameters. Likewise, the Kwei  
35 model, known to take into account hydrogen bonding interactions between monomers, could  
36 not describe well the evolution of  $T_g$ , indicating the existence of other factors influencing  $T_g$ .  
37 Finally, a thermodynamic approach based on entropy considerations allowed to attribute an  
38 explanation of the evolution of  $T_g$ .

39

## 40 INTRODUCTION

41 Improvement of thermal and mechanical properties of a polymeric material can be achieved  
42 by associating two or more polymers (copolymer, terpolymer, etc.).<sup>1-4</sup> However, combining  
43 several amorphous polymers possessing different structural units can influence the glass  
44 transition temperature ( $T_g$ ).<sup>5-7</sup> The latter is considered as a specific major transition for each  
45 polymeric material which determines its field of practical applications such as adhesives or  
46 coatings. The  $T_g$  represents a critical temperature beyond which the translational movement of  
47 the polymer chain is active. At this temperature, a transition from the glassy state to the  
48 rubbery state takes place, defining thus the range of operating temperatures of the material.<sup>8</sup>  
49 Below  $T_g$  the polymer chains in their amorphous state are frozen; only vibrational movements  
50 are active in this state. From a practical point of view, different common techniques allow to  
51 determine  $T_g$  experimentally, such as: DSC (Differential Scanning Calorimetry),<sup>9</sup> DMA  
52 (Dynamic Mechanical Analysis),<sup>10</sup> FTIR (Fourier Transform Infrared Spectroscopy).<sup>11</sup>  
53 Recently much interest was given to acrylic copolymers based on isobornylacrylate (IBOA),  
54 since various applications are possible in different domains.<sup>12,13a,14-16</sup> Poly(IBOA) has a large  
55 cyclic side group providing stiffness, low absorption and a relatively high  $T_g$  well above  
56 ambient temperature, which is situated close to that of poly(methylmethacrylate) (PMMA)  
57 and poly(styrene).<sup>17</sup> A literature survey unveils that only a few studies have been carried out  
58 to examine thermal properties of IBOA copolymers. In a recent report, Ko *et al.* described an  
59 increase of the thermal resistance by introducing isobornylmethacrylate (IBOMA) into poly  
60 (MMA-co-cyclohexylmaleimide), thus creating a ter-copolymer.<sup>12</sup> Jakubowski *et al.*  
61 investigated the thermal behavior of poly (IBOA-co-n-butylacrylate) by varying the ratio of  
62 IBOA and n-butylacrylate monomers.<sup>18</sup> DSC studies have revealed that these copolymer  
63 systems exhibit unique glass transition temperatures indicating the absence of phase  
64 separation effects. In this work thermal properties of photochemically elaborated linear and

65 crosslinked poly (IBOA-co-Isobutylacrylate) were examined experimentally by DSC  
66 measurements as function of initial monomer composition. Isobutylacrylate (IsoBA) was  
67 selected as co-monomer together with IBOA due to the large difference between the  $T_g$ 's of  
68 the two corresponding homopolymers. The  $T_g$  of poly (IBOA-co-IsoBA) could thus be varied  
69 over a wide range of temperatures, which might be useful for specific temperature dependent  
70 applications such as coatings with antibacterial and antimicrobial adhesion properties.<sup>15,16</sup>  
71 Indeed, these reports show that the resistance of polyurethanes at low temperature could be  
72 considerably improved by modulating the  $T_g$  of the polymer. This was achieved by  
73 incorporation of IBOA in the polymer, yielding a high-performance antibacterial material.<sup>16</sup>  
74 An attempt was made to describe the obtained experimental  $T_g$  data of linear and crosslinked  
75 poly (IBOA-co-IsoBA) applying theoretical models, by performing adjustment procedures  
76 (fitting) using data analysis software Origin and R.

### 78 **Theoretical approaches to describe the evolution of $T_g$**

79 Different approaches, such as those based on kinetical and/or thermodynamical considerations  
80 have been proposed to describe the dependence of  $T_g$  on the sample composition, mainly of  
81 polymer blends.<sup>19-29</sup> These models rely generally on the additivity of the properties of the  
82 components of the mixture. For example, Weng *et al.*<sup>19</sup> studied the effect of salt on  $T_g$  of  
83 sugars using Fox<sup>20</sup> and Gordon and Taylor (G-T)<sup>21</sup> models to describe their thermal behavior.  
84 Kuo *et al.*<sup>22</sup> applied the G-T approach to predict  $T_g$  of Poly (MAAM-co-MMA). The Fox  
85 equation is expressed as

$$86 \quad \frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{x_2}{T_{g,2}} \quad (1)$$

87 where  $T_g$  and  $T_{g,i}$  represent the glass transition temperatures of the mixture and of their pure  
88 components  $i$  ( $i=1,2$ ), and  $x_i$  is the mass fraction of component  $i$ . The G-T equation, which is  
89 based on the additivity rule of specific volumes of a two-component system (1 and 2), has

90 proved its reliability in predicting  $T_g$  values of blends of linear polymers and mixtures of  
91 polymers with plasticizers :

92 
$$\text{-----} \quad (2)$$

93 where  $K_{G-T}$  represents the G-T constant, which was evaluated applying the Simha-Boyer  
94 rule<sup>27,28</sup>

95 
$$\text{-----} \quad (3)$$

96 where  $\rho_1$  and  $\rho_2$  stand for the volume densities of components 1 and 2, respectively.

97 The Couchman-Karas (C-K) equation<sup>23,24</sup> has been developed on the basis of the classical  
98 thermodynamic theory, considering that the binary system behaves purely conformational.

99 This approach, assuming that the glass transition represents a thermodynamic event, weights  
100 the  $T_g$  of the single components by the change in heat capacity ( $\Delta C_p$ ) instead of the volume  
101 change occurring at the  $T_g$  of the binary system.  $\Delta C_{p1}$  and  $\Delta C_{p2}$ , corresponding to the isobaric  
102 heat capacity increments of pure components 1 and 2, are supposed to be temperature  
103 independent. The C-K equation can be written as follows :

104 
$$\text{-----} \quad (4)$$

105 Kwei<sup>25</sup> demonstrated that the evolution of  $T_g$  of mixtures of linear polymers might deviate  
106 from the G-T equation, due to specific interactions related to the presence of hydrogen bonds  
107 between the components. Kwei modified the G-T equation by introducing a second  
108 parameter,  $q$ , to take into account these interactions :

109 
$$\text{-----} \quad (5)$$

110 The  $K_{KW}$  constant is defined in the same way as  $K_{G-T}$ .

111

## 112 **EXPERIMENTAL**

### 113 **Materials**

114 IsoBA, IBOA, and the crosslinking agent 1,6-hexanedioldiacrylate (HDDA) were purchased  
115 from Sigma-Aldrich (Saint-Quentin Fallavier, France). The photoinitiator used was 2-  
116 hydroxy-2-methyl-1-phenyl-propane-1 (commercial designation: Darocur 1173), also  
117 obtained from Sigma-Aldrich.

118

### 119 **Sample preparation**

120 Linear poly(BOA-co-IsoBA) copolymers were prepared as function of composition of the  
121 mono-functional monomers IsoBA and IBOA. Copolymer networks with different cross-  
122 linking densities were elaborated as well, using the same monomers together with HDDA  
123 concentrations comprised between 0.1 and 0.7 weight-% (wt-%). The amount of  
124 photoinitiator was kept constant for all samples at 0.5 wt-% of the total monomeric blend.  
125 Mixtures of the monomers were stirred for 3 hours to homogenize the solutions, and then  
126 these blends were put in Teflon molds and exposed to UV-visible radiation with a wavelength  
127 of 365 nm and an intensity of 1.5 mW / cm<sup>2</sup>. These free radical copolymerization/crosslinking  
128 reactions were carried out under nitrogen to prevent inhibition effects, and the exposure time  
129 was set to 35 min to achieve complete conversion of all reactive acrylic monomers in the  
130 precursor systems. The copolymer samples obtained were optically transparent with variable  
131 rigidity at room temperature, i.e. an increase of stiffness was observed for samples with  
132 increasing amount of IBOA.

133 Figure 1 represents schematically the sample preparation route for the two copolymer  
134 architectures which have been investigated, i.e. linear and photochemically crosslinked  
135 poly(BOA-co-IsoBA).

136  
137

138 **Figure 1.** Elaboration of linear and photochemically crosslinked poly(IBOA-co-IsoBA).

139

140 *Determination of molar weight by size exclusion chromatography*

141 Size exclusion chromatography (SEC) measurements were performed at room temperature on  
142 a Waters Alliance e2695 system using THF as solvent (flow rate = 1 mL / min) and equipped  
143 with three columns placed in series (Styragel HR1, Styragel HR3, Styragel HR4). A Wyatt RI  
144 (differential refractive index) detector and a Wyatt MALS (Multi Angle Light Scattering)  
145 detector (laser  $\lambda = 670$  nm) were coupled to the system. Calibration was established with  
146 polystyrene (PS) standards from Polymer Laboratories.

147

148 *Thermal properties investigated by differential scanning calorimetry*

149 Thermal properties of the obtained homo- and copolymers were studied by DSC (Perkin-  
150 Elmer model 8000). The instrument was calibrated with indium and zinc as standards,  
151 applying a heating rate of 10°C / min. All experiments were conducted under nitrogen flow



152 (20 mL / min). Samples were prepared by introducing about 8-10 mg from arbitrary positions  
153 of the disk-shaped polymer samples into aluminum DSC crucibles.

154  $T_g$  was observed as a baseline shift related to a heat capacity change ( $\Delta C_p$ ) of the sample. It is  
155 well-known that measurement of  $T_g$  depends to a great extent on experimental parameters,  
156 such as heating and cooling rates. In order to obtain coherent  $T_g$  results for various amorphous  
157 copolymers in this work, a rate of 10°C / min (heating and cooling cycles) was applied in the  
158 temperature range from -72°C to 120°C. The program consisted first in cooling the sample,  
159 followed by three heating and cooling cycles to take into account eventual thermal events  
160 related to the sample preparation history. A Pyris computer software from Perkin-Elmer was  
161 used to determine  $T_g$  from the midpoint of the transition range of the thermograms. Only  
162 thermograms from the second heating scan were considered for the analysis.

163

#### 164 *Analysis by FTIR spectroscopy*

165 Fourier Transform Infrared spectra (FTIR) of the elaborated linear polymer films were  
166 recorded in Attenuated Total Reflection (ATR) mode at room temperature on a Perkin Elmer  
167 Frontier spectrometer in the wavenumber range between 4000 cm<sup>-1</sup> and 600 cm<sup>-1</sup> with a  
168 spectral resolution of 4 cm<sup>-1</sup> applying 32 scans.

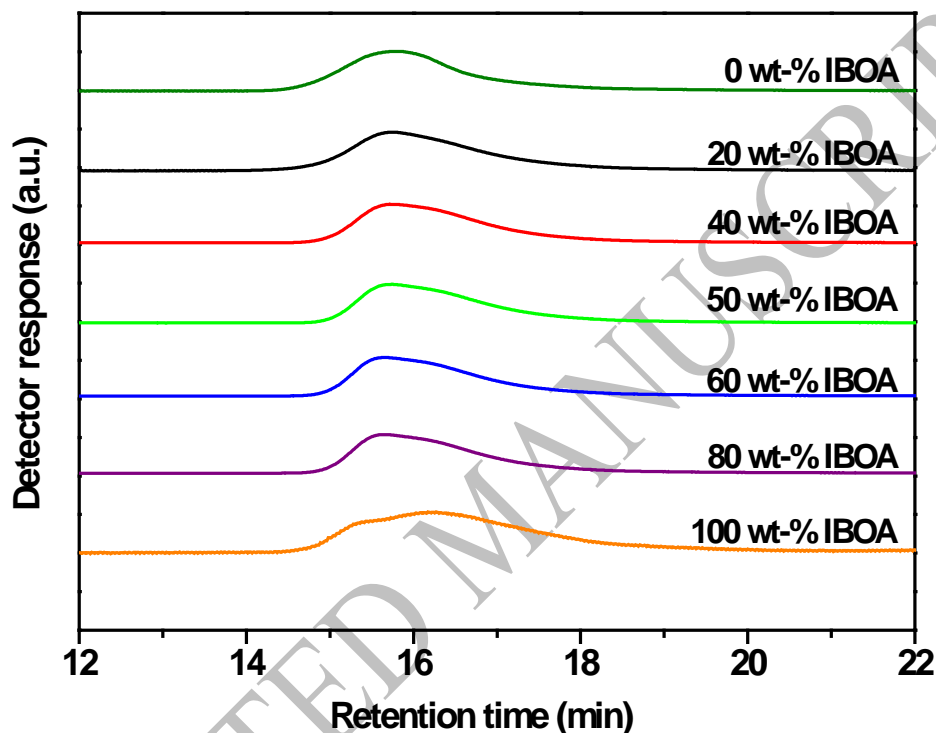
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## 170 **RESULTS AND DISCUSSION**

### 171 **Characterization of Poly(IBOA-co-IsoBA)**

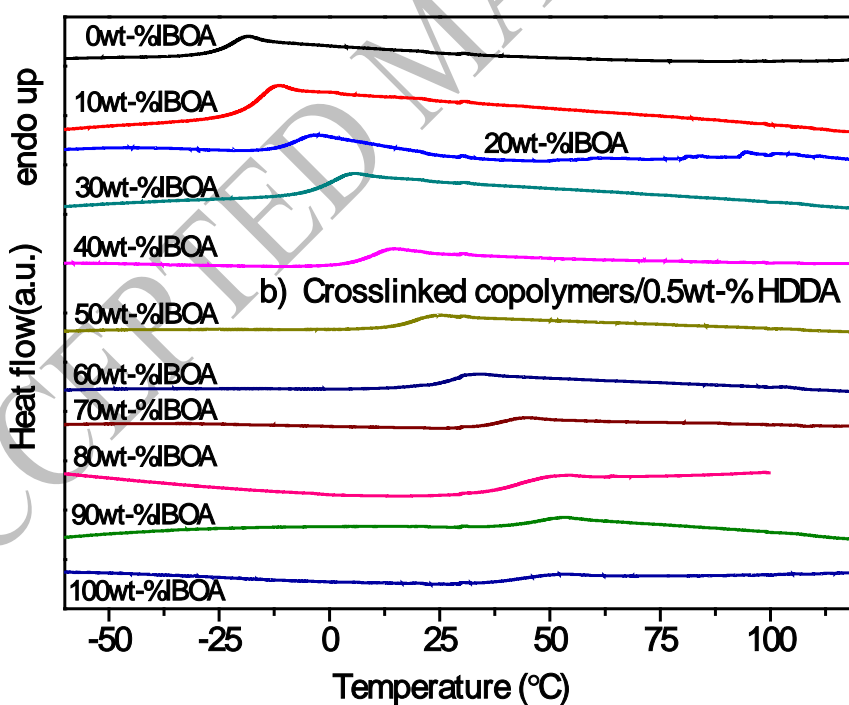
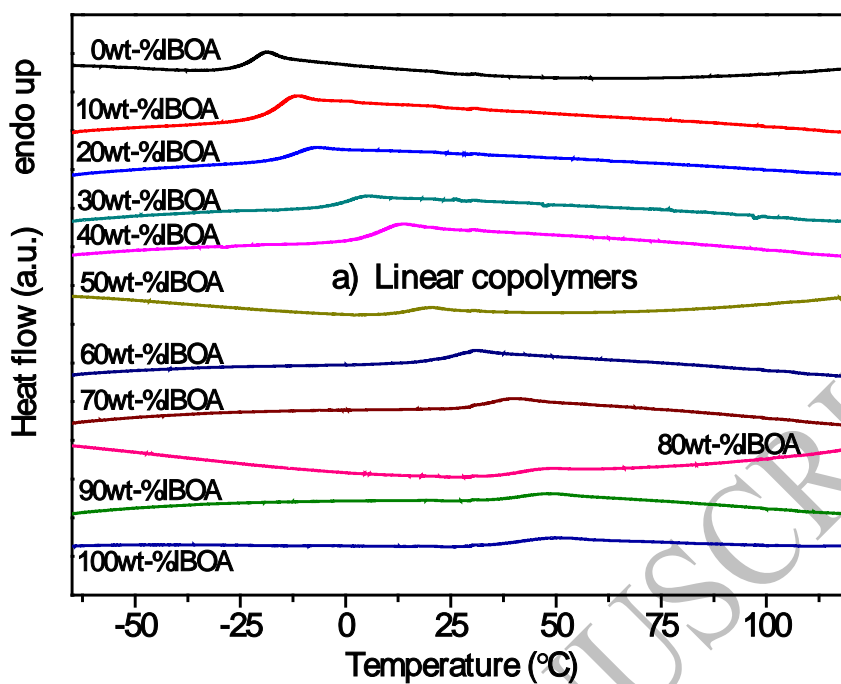
172 The technique of free radical photopolymerization was applied to elaborate linear and  
173 crosslinked Poly(IBOA-co-IsoBA) samples. The crosslinking degree was changed for the  
174 latter by adding different small amounts of HDDA as crosslinking agent into the initial  
175 monomeric blends. The structure of all elaborated copolymers was evidenced by immersion  
176 of the polymerized samples in a good organic solvent, Tetrahydrofuran (THF). Chemically

177 crosslinked polymer networks have indeed been formed for compositions containing HDDA,  
178 i.e. the disk-shaped samples immersed in THF present strong swelling effects, but did not  
179 dissolve in the presence of the solvent. On the other hand, the elaborated linear copolymers  
180 were found to be perfectly miscible in THF thus confirming their linear structure.



181  
182 **Figure 2.** Dependence of copolymer composition on SEC measurements for linear Poly  
183 (IBOA-co-IsoBA) samples.

184  
185 Figure 2 presents elugrams from SEC measurements for linear Poly (IBOA-co-IsoBA), as a  
186 function of copolymer composition. Some broadening of the molecular weight distribution  
187 could be observed with increasing IBOA content, but the average molecular weight of all  
188 copolymers remain roughly constant, indicating that the experimental results obtained from  
189 analysis of thermal properties do not depend on eventual differences in molecular weight.



190

191

192

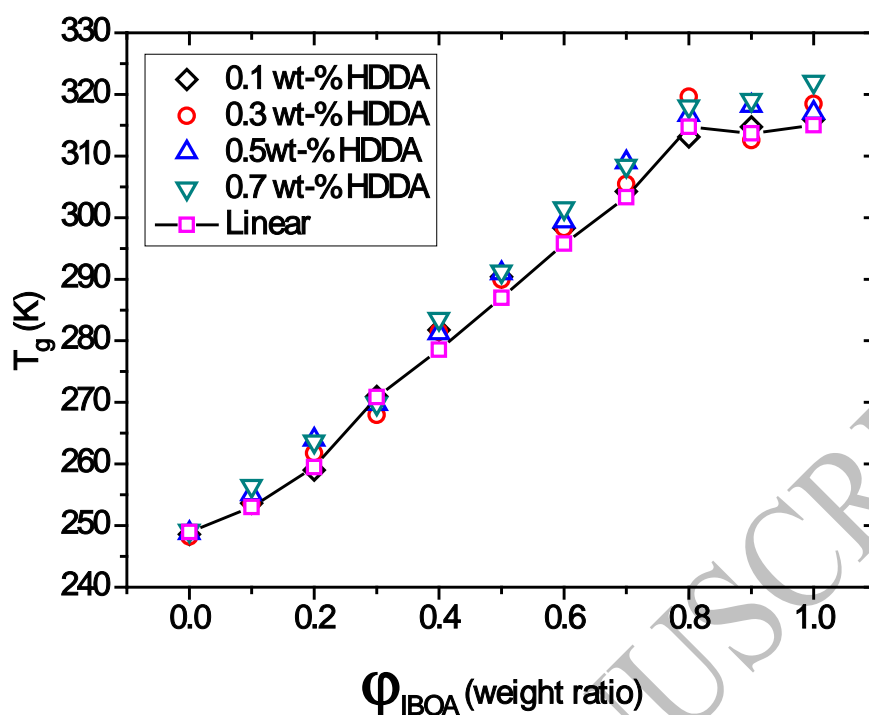
193 **Figure 3.** Thermograms obtained by DSC as functions of temperature and weight percentage  
 194 of IBOA for (a) linear Poly(IBOA-co-IsoBA) and (b) Poly (IBOA-co-IsoBA), crosslinked

195 with 0.5 wt-% HDDA.<sup>13b</sup>

196

197 Figure 3 shows the thermograms of linear [Figure 3(a)] and photochemically crosslinked  
198 [Figure 3(b)] Poly(IBOA-co-IsoBA) samples as function of the initial monomer composition,  
199 acquired by DSC measurements. Interestingly, only one single glass transition was observed  
200 as thermal event for all samples, on the temperature range explored between -72°C and  
201 120°C. Since only one glass transition was observed for all copolymer samples, it can be  
202 deduced that the analyzed systems could be considered as miscible from a thermodynamical  
203 point of view.<sup>24</sup> Semi-miscible and immiscible copolymers generally show two  $T_g$  values  
204 independent of the sample composition, corresponding to the  $T_g$ 's of their respective pure  
205 components. Figure 3 reveals that the  $T_g$  values increase significantly with the increase of the  
206 wt-% of IBOA in the copolymer. In particular,  $T_g$  changes from -24°C to 41°C, when  
207 increasing the amount of IBOA from 0 wt-% to 100 wt-% in the case of linear copolymers  
208 [Figure 3(a)]. In the same way the  $T_g$  values increase from -24°C to 43.9°C when increasing  
209 the amount of IBOA from 0 wt-% to 100 wt-% for copolymers crosslinked with 0.5 wt-% of  
210 HDDA [Figure 3(b)].

211 Figure 4 presents experimentally obtained  $T_g$  data for all linear and crosslinked Poly(IBOA-  
212 co-IsoBA), following an "S"-shaped form as function of sample composition. Interestingly,  
213 the  $T_g$  values obtained for linear copolymers appear to be close to those of the networks  
214 prepared using 0.1 wt-% up to 0.7 wt-% HDDA.



215

216 **Figure 4.** Evolution of the single glass transition temperature as function of the weight ratio  
 217 of the IBOA monomer for linear and crosslinked Poly (IBOA-co-IsoBA). Experimental error  
 218 bars are all smaller than the size of the data point symbols. The continuous line represents a  
 219 guide to the eye.

220

221 The data presented in Table 1 allow a more detailed analysis of the dependence of  $T_g$  on  
 222 composition and structure of the copolymers. Within the limits of experimental errors, a slight  
 223 tendency of increasing  $T_g$  values can be observed especially for higher IBOA concentrations  
 224 when comparing the case of linear Poly (IBOA-co-IsoBA) with the crosslinked copolymers in  
 225 the following order 0.1 wt-% / 0.3 wt-% / 0.5 wt-% / 0.7 wt-% HDDA in the precursor blends.

226

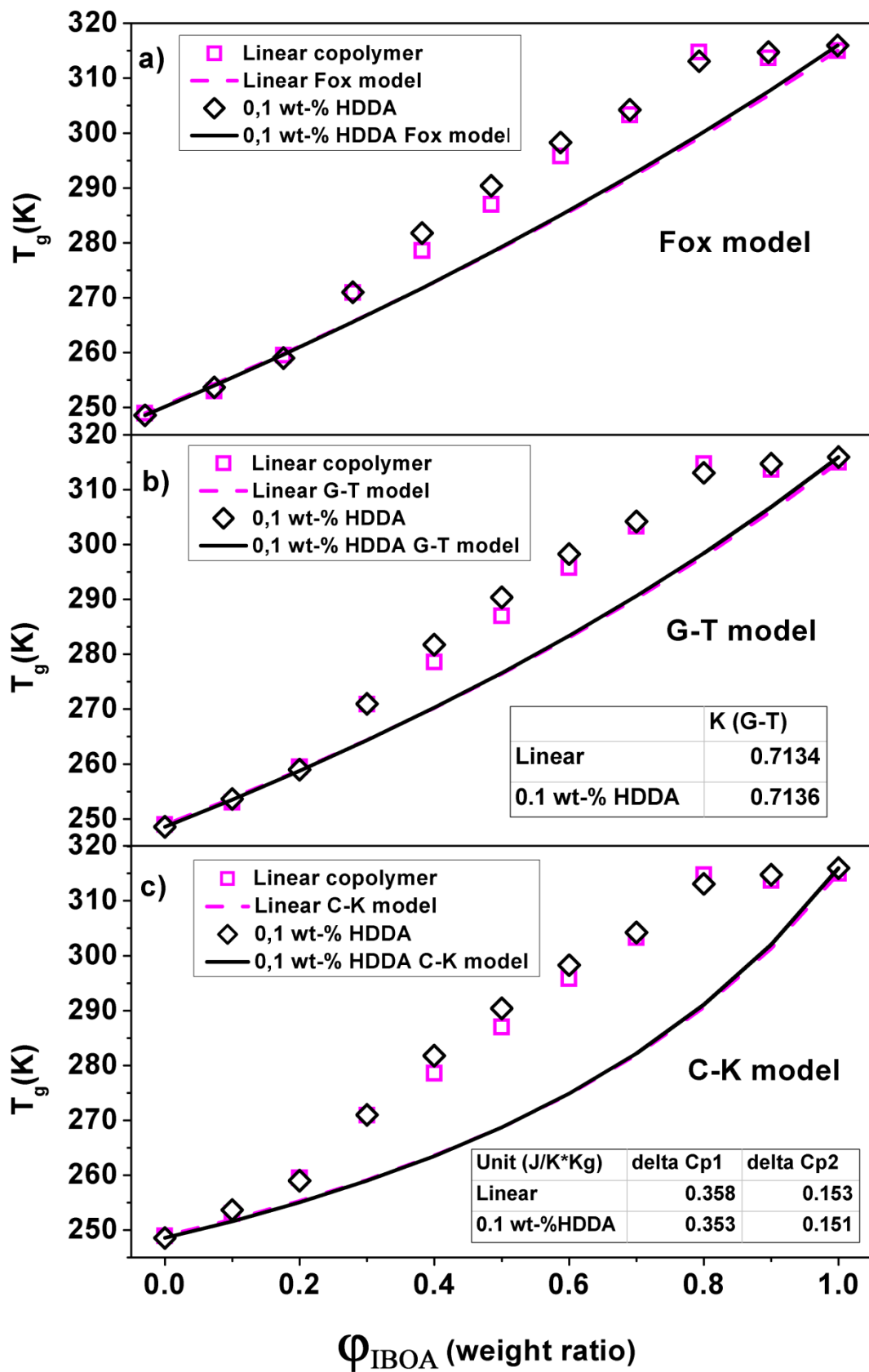
Composition	Linear	0.1 wt-%	0.3 wt-%	0.5 wt-%	0.7 wt-%
IBOA (wt-%)	$T_g$ (K)	HDDA	HDDA	HDDA	HDDA
		$T_g$ (K)	$T_g$ (K)	$T_g$ (K)	$T_g$ (K)
0	248.9	248.5	248.2	249.1	249.1
10	252.9	253.5	253.5	255.0	253.5
20	259.4	258.9	261.7	263.9	263.6
30	270.8	270.9	267.9	269.7	269.7
40	277.5	281.7	281.4	281.2	283.5
50	286.9	290.5	289.9	290.9	291.2
60	295.7	298.2	298.3	299.9	301.5
70	303.3	304.2	305.3	308.6	308.4
80	314.7	313.0	311.5	316.6	318.0
90	313.6	314.7	312.5	318.1	319.1
100	314.9	315.9	318.4	317.0	322.0

227

228 **Table 1.** Comparison between experimentally measured glass transition temperatures of linear  
 229 and crosslinked Poly (IBOA-co-IsoBA).

230

231 Nevertheless, since these thermal events were found to be rather similar for both copolymer  
 232 structures, theoretical models were applied on linear and on crosslinked Poly (IBOA-co-  
 233 IsoBA) as well, to describe the evolution of  $T_g$  as function of sample composition. The  
 234 applied theoretical approaches, which have been originally established for linear binary  
 235 systems, take into account the equations developed by Fox, G-T, C-K, and Kwei. For the sake  
 236 of simplicity, only the outcome from linear Poly (IBOA-co-IsoBA) and the crosslinked system  
 237 with 0.1 wt-% HDDA were presented here.



239 **Figure 5.** Evolution of  $T_g$  as a function of weight ratio of IBOA: Comparison of the  
240 experimental results with data calculated using the following equations (a) Fox, (b) Gordon  
241 and Taylor (G-T), and (c) Couchman and Karasz (C-K), for linear and crosslinked Poly  
242 (IBOA-co-IsoBA) with 0.1 wt-% of HDDA.

243

## 244 **Theoretical description of the glass transition temperature**

### 245 *Models without adjustment procedure*

246 The evolution of  $T_g$  of binary copolymers as function of sample composition has been  
247 described in literature by Fox,<sup>20</sup> G-T,<sup>21</sup> and C-K.<sup>23</sup> Figure 5 presents experimental data and  
248 values calculated according to these approaches without applying an adjustment procedure,  
249 for linear and crosslinked Poly (IBOA-co-IsoBA) with 0.1 wt-% of HDDA. Figure 5(a) shows  
250 that the Fox equation fail to describe the evolution of  $T_g$  as a function of sample composition,  
251 probably due to strong asymmetric contributions of polymeric IBOA and IsoBA. A  
252 comparison of experimental data with results calculated from the G-T approach is presented  
253 in Figure 5(b), yielding only a fair description of the experiments. Figure 5(c) shows a rather  
254 strong discrepancy between theory and experiments, by application of the C-K model.

255

### 256 *Models applying an adjustment procedure*

257 Origin and R softwares were applied to carry out adjustment (fitting) procedures (least  
258 squares method) of parameter values included in the models of G-T [Eq. (2)], C-K [Eq. (4)],  
259 and Kwei [Eq. (5)]. Obviously application of adjustment procedures leads to a better but not  
260 perfect description of the experimental data as can be seen on Figure 6(a), where the  $K_{GT}$   
261 parameter from the G-T model was determined as 0.73 and 0.68 for linear and cross-linked  
262 Poly (IBOA-co-IsoBA) with 0.1 wt-% HDDA, respectively. Similar remarks can be made for  
263 the C-K model shown in Figure 6(b). A better adjustment of the theoretical description to the

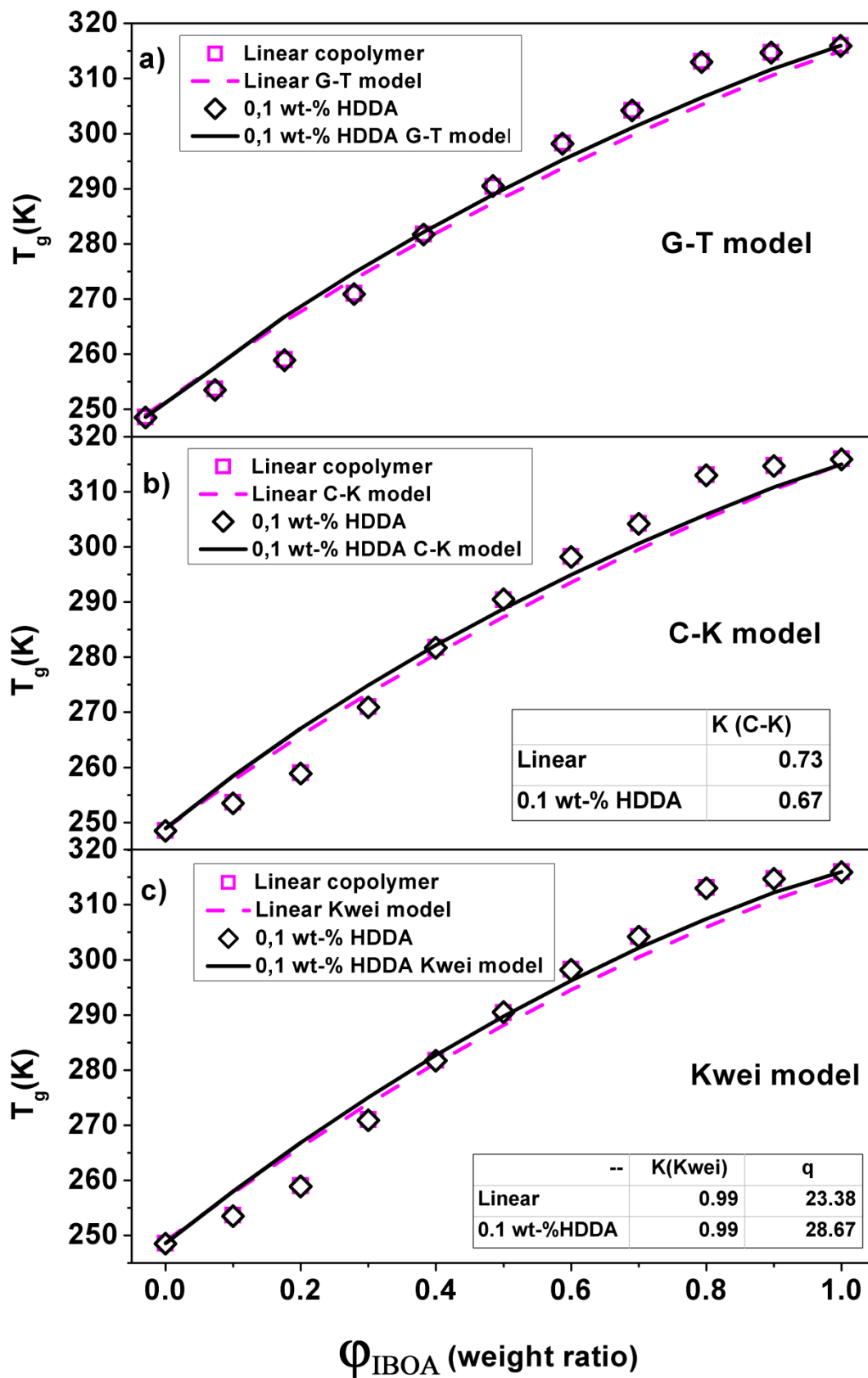


264 experimental data was observed compared to the model without adjustment parameter.  $K_{C-K}$   
265 was found equal to 0.73 and 0.67 for the linear copolymer and the crosslinked Poly (IBOA-  
266 co-IsoBA) with 0.1 wt-% HDDA, respectively. These values suggest that IBOA is slightly  
267 dominant in its contribution to the  $T_g$  of the copolymer. While the G-T model describe well  
268 the experimental data between 0.4 wt-% and 0.7 wt-% IBOA, the adjustment becomes less  
269 efficient when approaching the extremities of the phase diagrams.

270 Application of the Kwei Eq. (5), containing an additional parameter ( $q$ ) to be adjusted, did not  
271 yield a better description of the experimental data than that obtained from the G-T and C-K  
272 equations [(Figure 6(c)]. The values of  $K_{KW}$  for both linear and crosslinked Poly (IBOA-co-  
273 IsoBA) with 0.1 wt-% of HDDA were found to be identical and close to 1, probably related to  
274 a limitation effect of the adjustment procedure. On the other hand the Kwei equation has  
275 already been successfully applied to describe a complex S-shaped evolution of  $T_g$  as function  
276 of composition as shown by Weng *et al.* for sugar-salt mixtures.<sup>19</sup> The situation here is  
277 different probably due to the fact that the S-shaped evolution is less pronounced in Figure 6(b)  
278 than in Ref. 19, requiring a fitting procedure involving more than 2 parameters to be adjusted.

279

ACCEPTED MANUSCRIPT



281 **Figure 6.** Results from modeling the evolution of  $T_g$  as a function of the weight ratio of IBOA  
282 by the equations of (a) Gordon and Taylor (G-T), (b) Couchman and Karasz (C-K), and (c)  
283 Kwei for linear and crosslinked Poly (IBOA-co-IsoBA) with 0.1 wt-% of HDDA.

284  
285 It can be concluded that the models applied above were not satisfactory to predict the  
286 compositional evolution of experimentally obtained  $T_g$  values of poly(IBOA-co-IsoBA). A  
287 possible source of discrepancies between theory and experiment could be the change of the  
288 entropy mixing term occurring at the transition from glassy to rubbery states, which was not  
289 considered by the previously used models. The presence of polymer chain units exhibiting  
290 different structural chain mobility like the rigid IBOA and the flexible IsoBA monomeric  
291 units in the copolymer might lead to deviations of the compositional dependencies of the  
292 entropic contributions. In order to take into account the contribution of the entropy change  
293 ( $\Delta S_{\text{mix}}$ ) at  $T_g$ , the approach from Pinal *et al.*<sup>30</sup> was applied, which provides a direct  
294 relationship between  $\Delta S_{\text{mix}}$  and  $T_g$  :

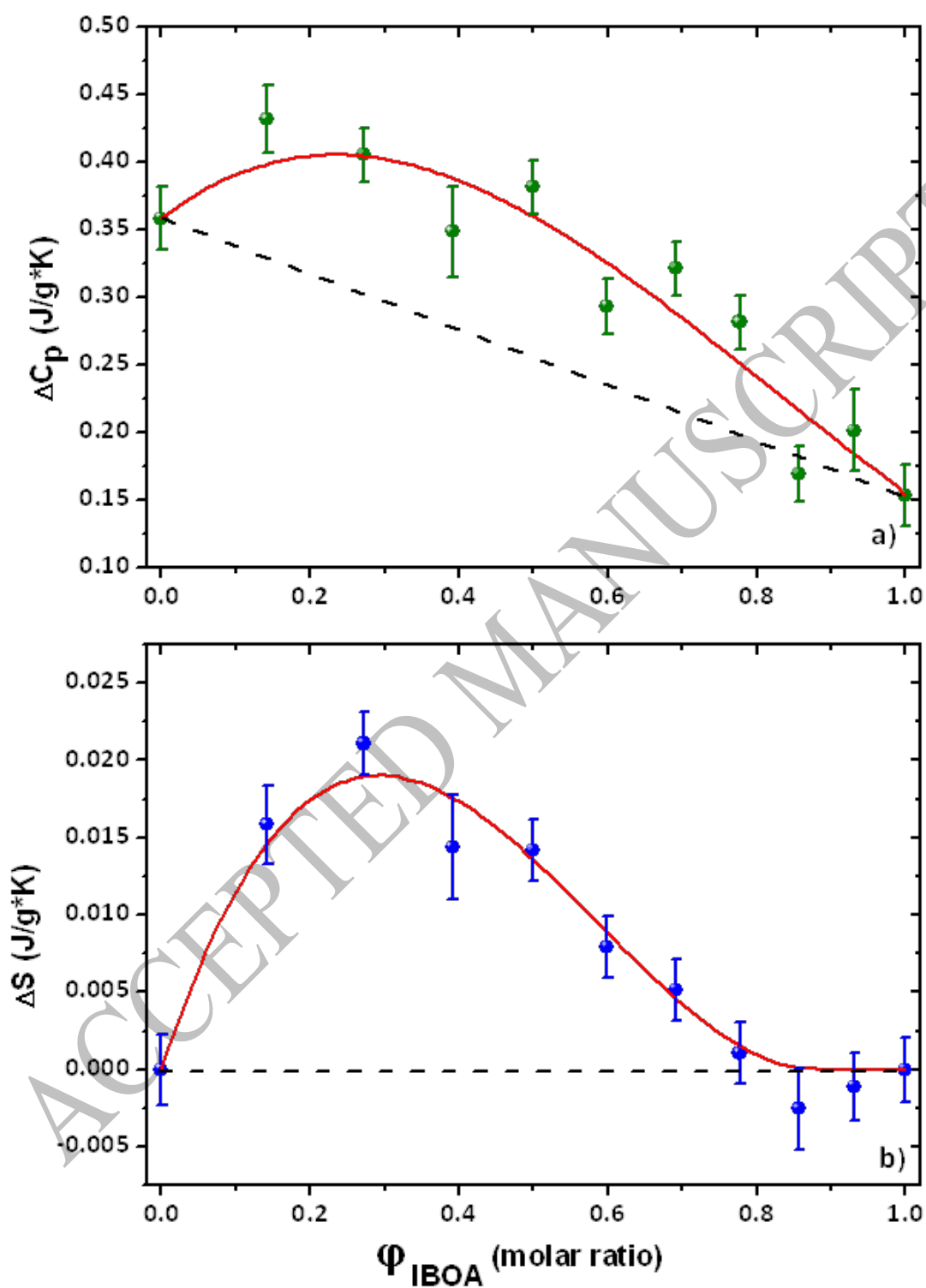
(6)

295 where  $T_{g,C-K}$  represents  $T_g$  of the copolymers obtained from the C-K model [Eq. (4)] and  
296  $\Delta C_{p,\text{mix}}$  stands for the composition dependent heat capacity change of the copolymers at the  
297 experimentally determined  $T_g$ 's. In order to calculate  $\Delta S_{\text{mix}}$ , Eq. (6) can be rewritten as  
298 follows:

(7)

299

300



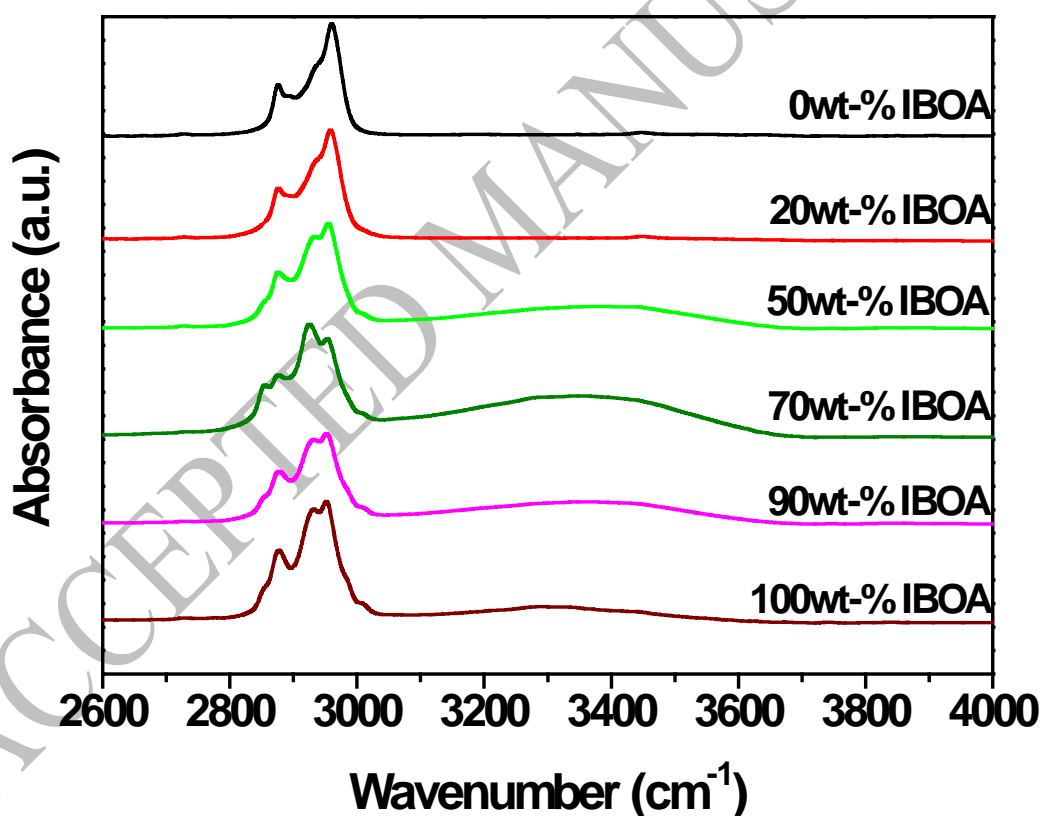
302 **Figure 7.** Composition dependence of a)  $\Delta C_{p,mix}$  and b)  $\Delta S_{mix}$  for linear poly(IBOA-co-  
303 IsoBA). The dashed straight lines between the data of the pure homopolymers poly(IBOA)  
304 and poly(IsoBA) correspond to the case  $\Delta S_{mix} = 0$ . The smooth lines represent guides for the  
305 eyes, and follow the data points.

306

307 The composition dependence of  $\Delta C_{p,mix}$  is plotted in Figure 7(a) for the case of linear poly  
308 (IBOA-co-IsoBA). The copolymer data exhibit a positive deviation from linearity which is  
309 given by a straight line between the two  $\Delta C_p$  values of the homopolymers, indicating the  
310 presence of specific interactions between IBOA- and IsoBA-units. Using the outcome of  
311 Figure 7(a),  $\Delta S_{mix}$  could be calculated following Eq. (7). Figure 7(b) represents  $\Delta S_{mix}$  as  
312 function of copolymer composition, exhibiting small positive entropy changes for copolymer  
313 compositions up to an IBOA molar fraction of 0.75.  $\Delta S_{mix}$  data above this molar fraction  
314 show values around 0 within the error bars. These results can be explained by the presence of  
315 specific inter- and intramolecular interactions, which increase with more enhanced chain  
316 mobility related to the increase of the amount of the flexible IsoBA in the copolymer. At  
317  $\phi_{IBOA} = 0.85$ ,  $\Delta S_{mix}$  presents a negative value due to a down-shifted data point of  $\Delta C_p$  in  
318 Figure 7(a), at the same molar fraction.  $\Delta S_{mix}$  could thus be considered either positive or zero  
319 for all copolymer compositions.

320 An attempt was made to seek for experimental evidence of the existence of IBOA and IsoBA  
321 interactions. In particular, the low frequency region of infrared spectra reveals, among others,  
322 vibrational modes of inter- and intramolecular hydrogen bonding. It is well-known that such  
323 interactions lead to significant changes of vibrational modes in the IR spectrum, like  
324 frequency shifts in the order of magnitude of hundreds of  $\text{cm}^{-1}$  and increases of IR intensity  
325 for bands related to vibrational modes of functional groups directly involved in the hydrogen-  
326 bonded bridges.

327 Infrared spectroscopic analysis by the ATR method was conducted at ambient temperature on  
328 linear Poly (IBOA-co-IsoBA) samples by varying the IBOA/IsoBA ratio in the precursor  
329 blends (Figure 8). For copolymers containing 50-90 wt-% IBOA, a broad absorbance band  
330 appeared in the low frequency region from 3100  $\text{cm}^{-1}$  to 3700  $\text{cm}^{-1}$ , characteristic for the O-H  
331 stretching region. Interestingly this band was absent in the case of the homopolymer Poly  
332 (IsoBA) and only a broad band of low intensity exhibiting a maximum around 3300  $\text{cm}^{-1}$  was  
333 observed for Poly (IBOA). Moreover, a shift of this maximum of approximately 100  $\text{cm}^{-1}$  to  
334 higher wavenumbers was observed by increasing the content of IsoBA within the copolymer



335  
336 **Figure 8.** Experimental evidence of the existence of hydrogen bonding interactions by ATR-  
337 FTIR spectroscopy analysis of linear Poly (IBOA-co-IsoBA).

338

339 from 0 to 80 wt-%. The intensity of this band increases from 0 to 30 wt-% IsoBA then  
340 decreases from 30 to 80 wt-% IsoBA. It can be assumed that hydrogen bonding interactions  
341 could occur between a positively charged hydrogen atom and an electronegative atom like  
342 oxygen from carbonyl groups. In the case of IBOA, Figure (6) of Ref. 31, presenting the  $^1\text{H}$ -  
343 NMR spectrum of linear Poly(IBOA), shows that the Methine proton  $\text{H}_9$  appears deshielded at  
344 4,6 ppm due to the vicinity of the carboxyl group, and might therefore be a good candidate for  
345 hydrogen bonding.

346 As a result, mobility of the main chain might be hindered by the existence of non-covalent  
347  $\text{O}\cdots\text{H}\cdots\text{O}\cdots\text{H}$  sequences among the side chains. This might also explain the relatively low  $T_g$   
348 value obtained for Poly(IBOA) (Figure 3) instead of  $T_g = 94^\circ\text{C}$ ,<sup>17</sup> in spite of the high  
349 molecular weight of Poly(IBOA). However, the  $\text{O}\cdots\text{H}$  sequences dissociate easily by  
350 increasing temperature. An evidence of gradual dissociation of the  $\text{O}\cdots\text{H}\cdots\text{O}\cdots\text{H}$  type of  
351 hydrogen-bonds with increasing temperature could we observed in the O-H stretching region  
352 (Figure 8), in relationship with the  $T_g$  dependence of the copolymer composition. Indeed,  $T_g$   
353 of copolymers including 50 wt-% and more of IBOA were found below ambient temperature  
354 and present hydrogen bonding interactions. On the other hand, copolymers with IBOA  
355 content lower than 50 wt-% present glass transitions above room temperature together with  
356 the absence of hydrogen bonding.

357

## 358 CONCLUSIONS

359 Linear and photochemically crosslinked poly(IBOA-co-isoBA) were successfully elaborated  
360 and characterized by GPC, FTIR and DSC techniques. A single glass transition was observed  
361 for all samples, and the graphical presentation of  $T_g$  as function of sample composition  
362 revealed a characteristic S-shaped form.

363 The equations of Fox-, G-T- and C-K-models, based on the assumption of free volume  
364 additivity, fail to describe the concentration dependant evolution of  $T_g$  of poly(IBOA-co-  
365 IsoBA), even if the  $K_{G-T}$  and  $K_{C-K}$  parameters were optimized using fitting procedures.  
366 Slightly better adjustment results were obtained using the Kwei approach providing a second  
367 adjustment parameter  $q$ . The discrepancies between theory and experiment could be removed  
368 by taking into account the entropy change of mixing presenting small positive values,  
369 indicating the presence of inter- and intramolecular interactions. In particular FTIR  
370 spectroscopic measurements carried out at ambient temperature confirmed the presence of  
371 strong hydrogen bonding particularly for intermediate IBOA/IsoBA compositions.

372

#### 373 **DECLARATION OF COMPETING INTEREST**

374 The authors declare that they have no known competing financial interests or personal  
375 relationships that could have appeared to influence the work reported in this paper.

376

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