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

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Abstract

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

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INTRODUCTION

Improvement of thermal and mechanical properties of a polymeric material can be achieved by associating two or more polymers (copolymer, terpolymer, etc.).[1-4] However, combining several amorphous polymers possessing different structural units can influence the glass transition temperature (T_g).[5-7] The latter is considered as a specific major transition for each polymeric material which determines its field of practical applications such as adhesives or coatings. The T_g represents a critical temperature beyond which the translational movement of the polymer chain is active. At this temperature, a transition from the glassy state to the rubbery state takes place, defining thus the range of operating temperatures of the material.[8] Below T_g the polymer chains in their amorphous state are frozen; only vibrational movements are active in this state. From a practical point of view, different common techniques allow to determine T_g experimentally, such as: DSC (Differential Scanning Calorimetry),[9] DMA (Dynamic Mechanical Analysis),[10] FTIR (Fourier Transform Infrared Spectroscopy).[11].

Recently much interest was given to acrylic copolymers based on isobornylacrylate (IBOA), since various applications are possible in different domains.[12,13a,14-16] Poly(IBOA) has a large cyclic side group providing stiffness, low absorption and a relatively high T_g well above ambient temperature, which is situated close to that of poly(methylmethacrylate) (PMMA) and poly(styrene).[17] A literature survey unveils that only a few studies have been carried out to examine thermal properties of IBOA copolymers. In a recent report, Ko *et al.* described an increase of the thermal resistance by introducing isobornylmethacrylate (IBOMA) into poly (MMA-co-cyclohexylmaleimide), thus creating a ter-copolymer.[12] Jakubowski *et al.* investigated the thermal behavior of poly (IBOA-co-n-butylacrylate) by varying the ratio of IBOA and n-butylacrylate monomers.[18] DSC studies have revealed that these copolymer systems exhibit unique glass transition temperatures indicating the absence of phase separation effects. In this work thermal properties of photochemically elaborated linear and crosslinked poly (IBOA-co-Isobutylacrylate) were examined experimentally by DSC measurements as function of initial monomer composition. Isobutylacrylate (IsoBA) was selected as co-monomer together with IBOA due to the large difference between the T_g's of the two corresponding homopolymers. The T_g of poly (IBOA-co-IsoBA) could thus be varied over a wide range of temperatures, which might be useful for specific temperature dependent applications such as coatings with antibacterial and antimicrobial adhesion properties.[15,16] Indeed, these reports show that the resistance of polyurethanes at low temperature could be considerably improved by modulating the T_g of the polymer. This was achieved by incorporation of IBOA in the polymer, yielding a high-performance antibacterial material.[16]

An attempt was made to describe the obtained experimental T_g data of linear and crosslinked poly (IBOA-co-IsoBA) applying theoretical models, by performing adjustment procedures (fitting) using data analysis software Origin and R.

Theoretical approaches to describe the evolution of T_g

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

$$— \quad — \quad — \qquad (1)$$

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

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

(2)

where $K_{G\text{-}T}$ represents the G-T constant, which was evaluated applying the Simha-Boyer rule[27,28]

(3)

where ρ_1 and ρ_2 stand for the volume densities of components 1 and 2, respectively.

The Couchman-Karasz (C-K) equation[23,24] has been developed on the basis of the classical thermodynamic theory, considering that the binary system behaves purely conformational. This approach, assuming that the glass transition represents a thermodynamic event, weights the T_g of the single components by the change in heat capacity (ΔC_p) instead of the volume change occurring at the T_g of the binary system. ΔC_{p1} and ΔC_{p2}, corresponding to the isobaric heat capacity increments of pure components 1 and 2, are supposed to be temperature independent. The C-K equation can be written as follows :

(4)

Kwei[25] demonstrated that the evolution of T_g of mixtures of linear polymers might deviate from the G-T equation, due to specific interactions related to the presence of hydrogen bonds between the components. Kwei modified the G-T equation by introducing a second parameter, q, to take into account these interactions :

(5)

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

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EXPERIMENTAL

Materials

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

Sample preparation

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

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

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

Determination of molar weight by size exclusion chromatography

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

Thermal properties investigated by differential scanning calorimetry

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

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

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

Analysis by FTIR spectroscopy

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

RESULTS AND DISCUSSION

Characterization of Poly(IBOA-co-IsoBA)

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

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

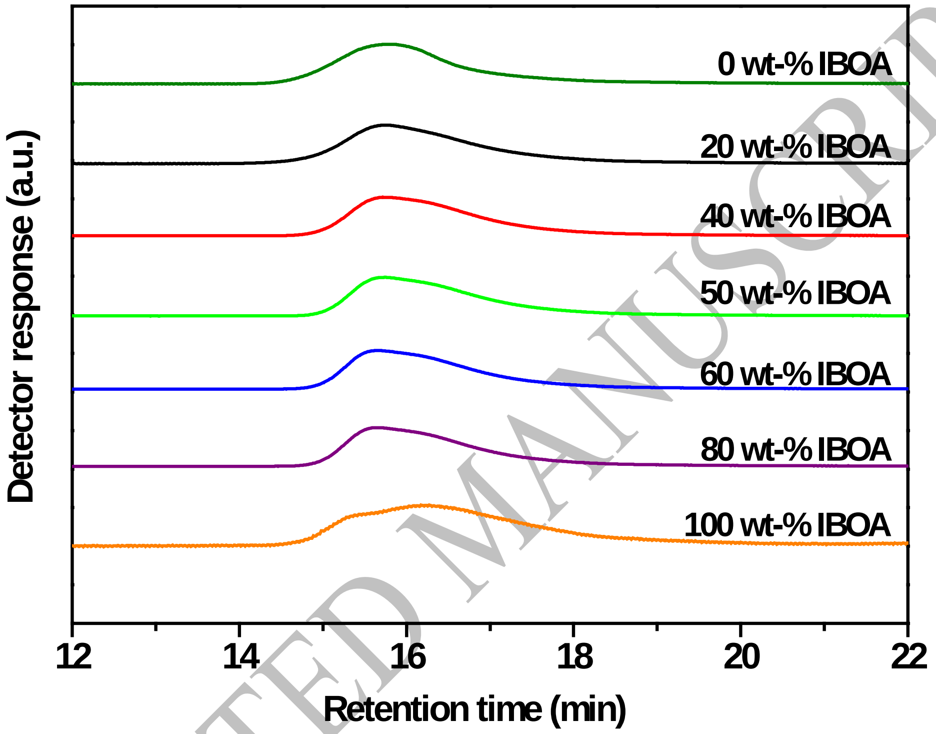

Figure 2. Dependence of copolymer composition on SEC measurements for linear Poly (IBOA-co-IsoBA) samples.

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

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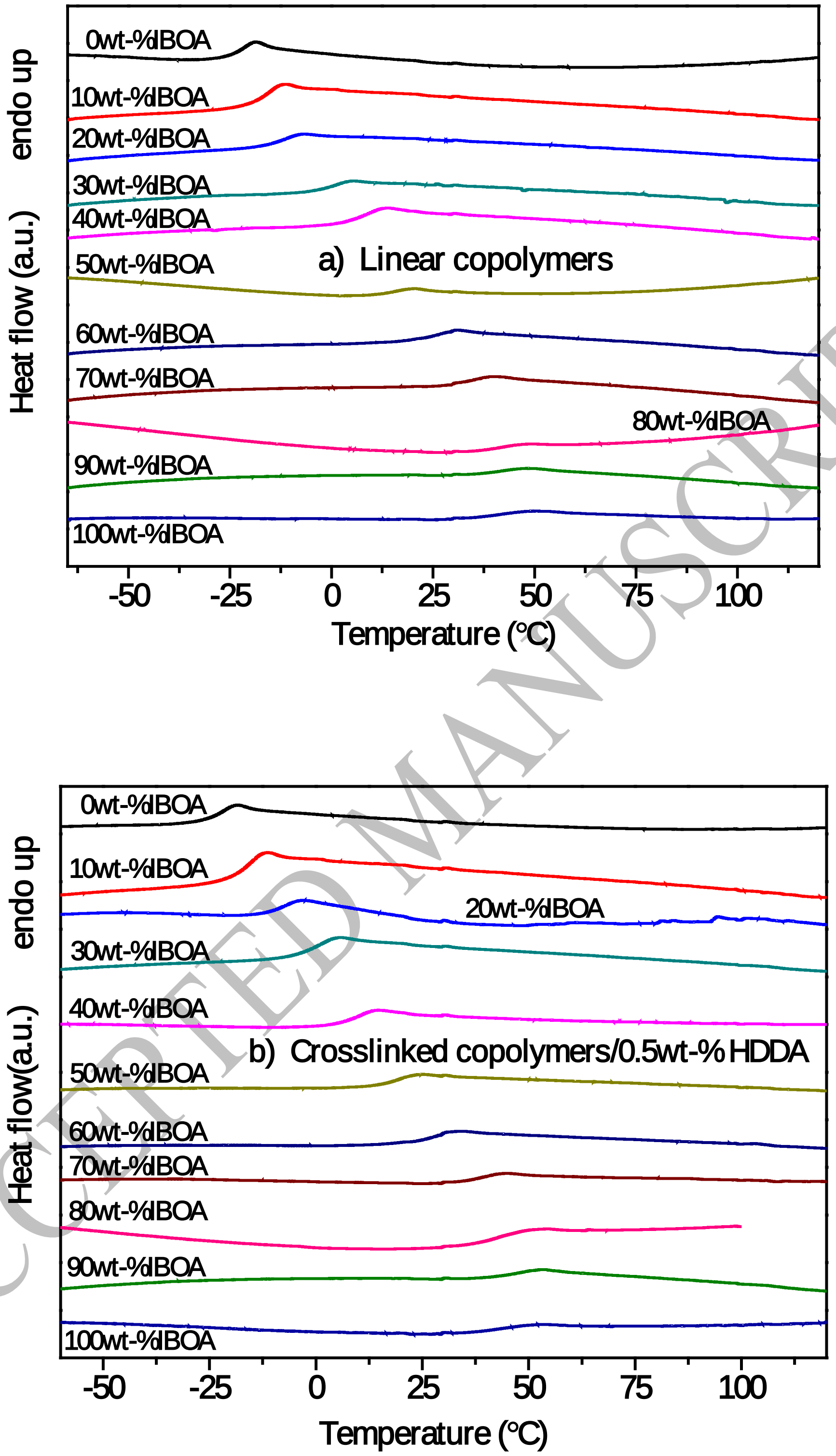

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Figure 3. Thermograms obtained by DSC as functions of temperature and weight percentage of IBOA for (a) linear Poly(IBOA-co-IsoBA) and (b) Poly (IBOA-co-IsoBA), crosslinked

with 0.5 wt-% HDDA.[13b]

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

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

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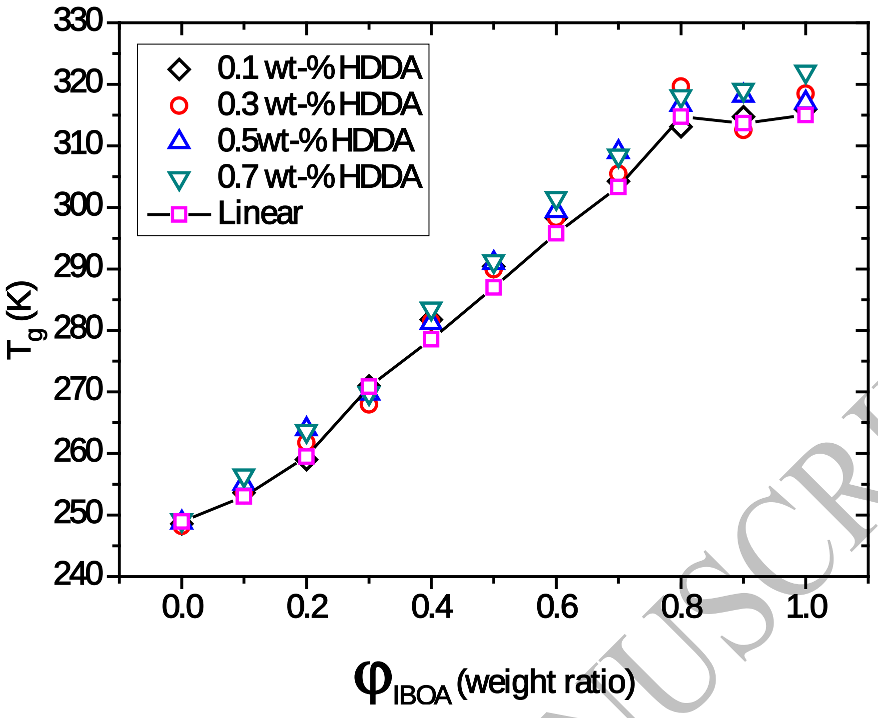

Figure 4. Evolution of the single glass transition temperature as function of the weight ratio of the IBOA monomer for linear and crosslinked Poly (IBOA-co-IsoBA). Experimental error bars are all smaller than the size of the data point symbols. The continuous line represents a guide to the eye.

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

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Composition IBOA (wt-%)	Linear T_g (K)	0.1 wt-% HDDA T_g (K)	0.3 wt-% HDDA T_g (K)	0.5 wt-% HDDA T_g (K)	0.7 wt-% HDDA 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

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

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

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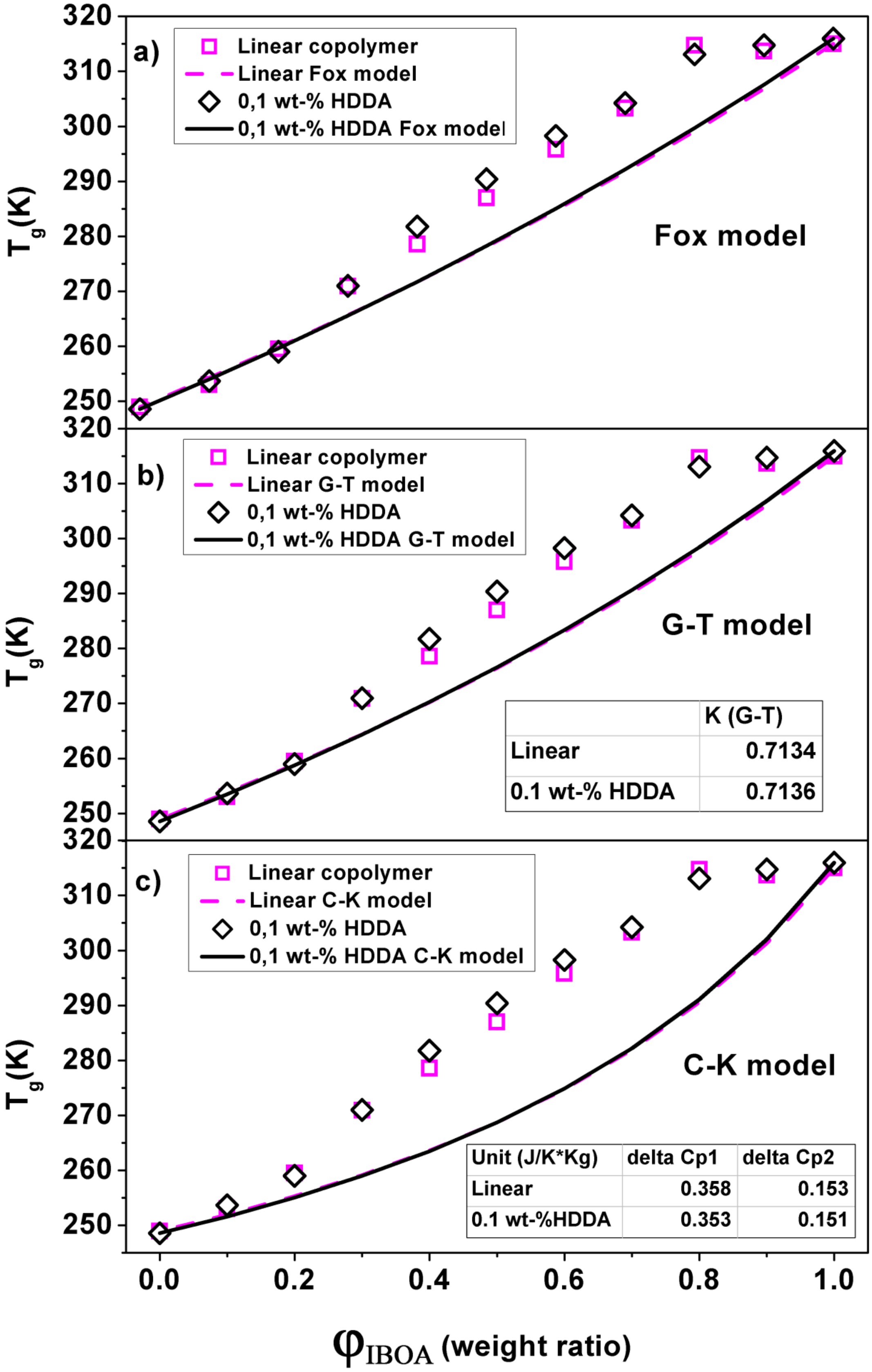

	K (G-T)
Linear	0.7134
0.1 wt-% HDDA	0.7136

Unit (J/K*Kg)	delta Cp1	delta Cp2
Linear	0.358	0.153
0.1 wt-%HDDA	0.353	0.151

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

Theoretical description of the glass transition temperature

Models without adjustment procedure

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

Models applying an adjustment procedure

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

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

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

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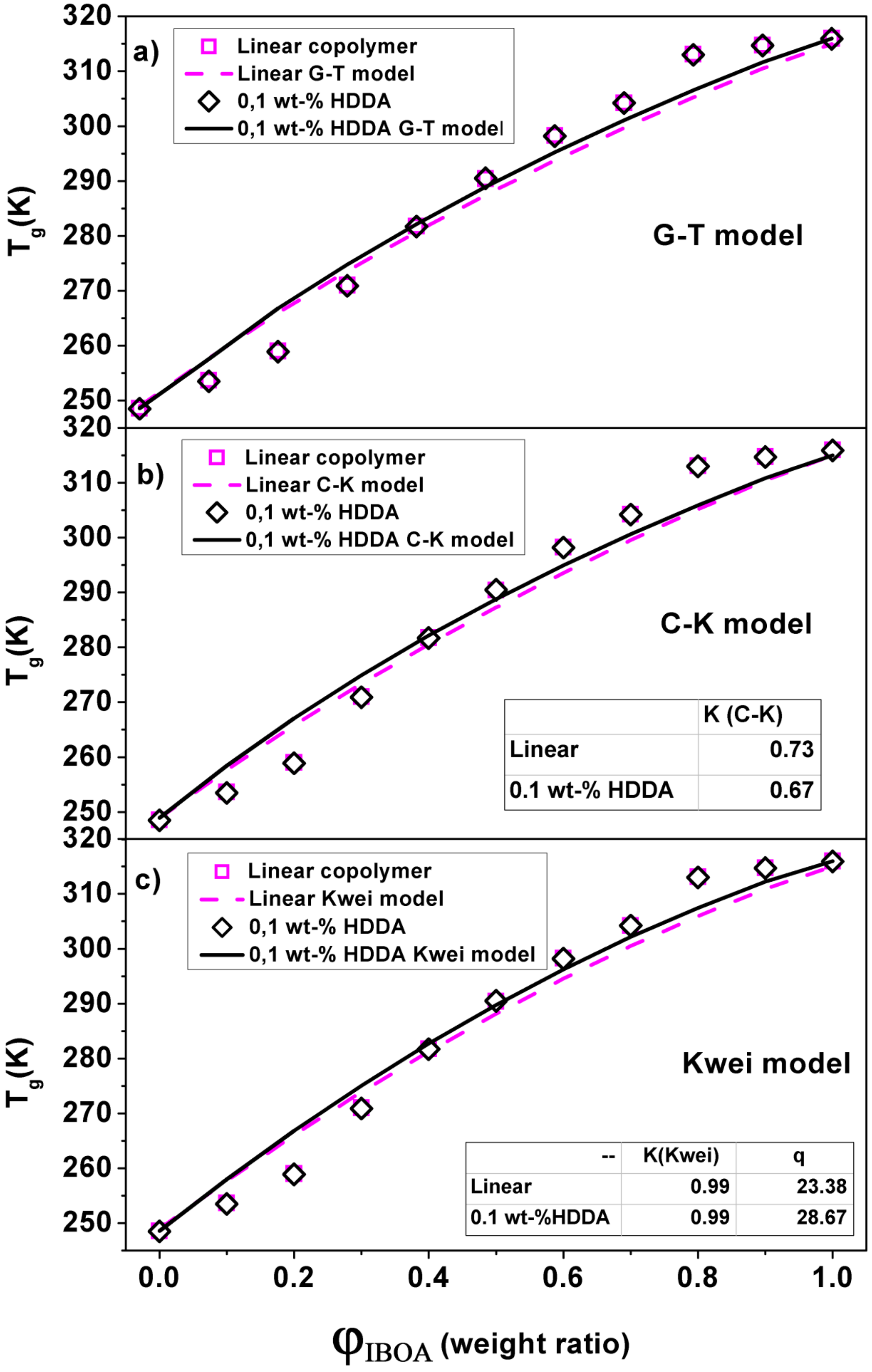
a)
Linear copolymer
Linear G-T model
0,1 wt-% HDDA
0,1 wt-% HDDA G-T model
G-T model
b)
Linear copolymer
Linear C-K model
0,1 wt-% HDDA
0,1 wt-% HDDA C-K model
C-K model
K (C-K)
Linear 0.73
0.1 wt-% HDDA 0.67
c)
Linear copolymer
Linear Kwei model
0,1 wt-% HDDA
0,1 wt-% HDDA Kwei model
Kwei model
-- K(Kwei) q
Linear 0.99 23.38
0.1 wt-%HDDA 0.99 28.67
T_g(K)
250
260
270
280
290
300
310
320
0.0
0.2
0.4
0.6
0.8
1.0
φ_{IBOA} (weight ratio)

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

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

(6)

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

(7)

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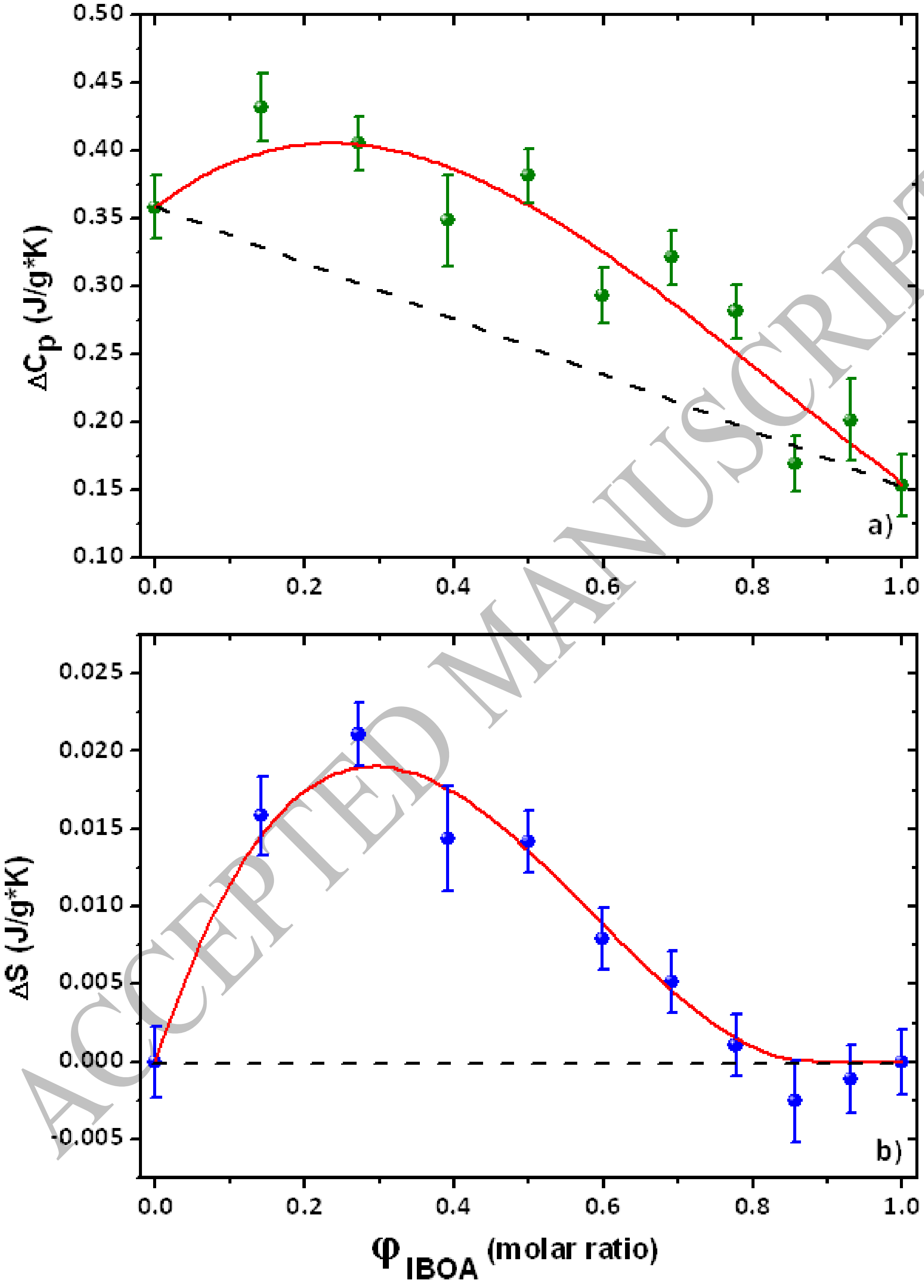

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Figure 7. Composition dependence of a) $\Delta C_{p,mix}$ and b) ΔS_{mix} for linear poly(IBOA-co-IsoBA). The dashed straight lines between the data of the pure homopolymers poly(IBOA) and poly(IsoBA) correspond to the case $\Delta S_{mix} = 0$. The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

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

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

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

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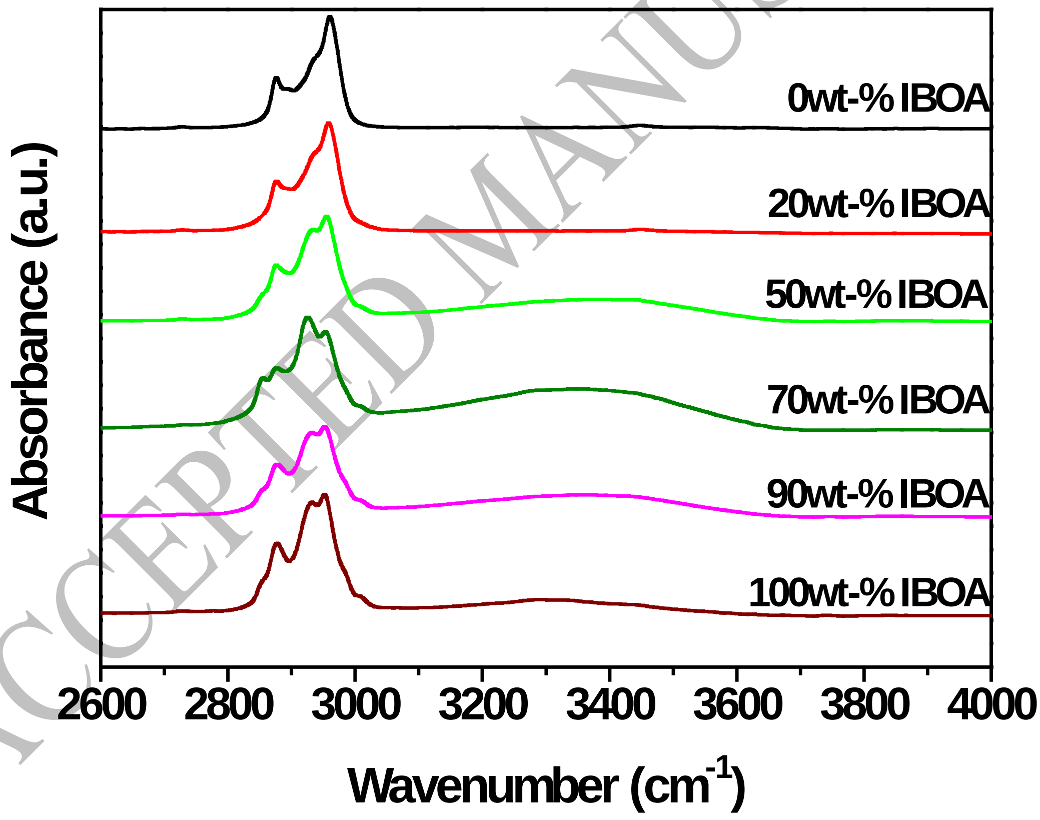

Figure 8. Experimental evidence of the existence of hydrogen bonding interactions by ATR-FTIR spectroscopy analysis of linear Poly (IBOA-co-IsoBA).

from 0 to 80 wt-%. The intensity of this band increases from 0 to 30 wt-% IsoBA then decreases from 30 to 80 wt-% IsoBA. It can be assumed that hydrogen bonding interactions could occur between a positively charged hydrogen atom and an electronegative atom like oxygen from carbonyl groups. In the case of IBOA, Figure (6) of Ref. 31, presenting the ^{1}H-NMR spectrum of linear Poly(IBOA), shows that the Methine proton H_9 appears deshielded at 4,6 ppm due to the vicinity of the carboxyl group, and might therefore be a good candidate for hydrogen bonding.

As a result, mobility of the main chain might be hindered by the existence of non-covalent O•••H•••O•••H sequences among the side chains. This might also explain the relatively low T_g value obtained for Poly(IBOA) (Figure 3) instead of T_g = 94°C,[17] in spite of the high molecular weight of Poly(IBOA). However, the O•••H sequences dissociate easily by increasing temperature. An evidence of gradual dissociation of the O•••H•••O•••H type of hydrogen-bonds with increasing temperature could we observed in the O-H stretching region (Figure 8), in relationship with the T_g dependence of the copolymer composition. Indeed, T_g of copolymers including 50 wt-% and more of IBOA were found below ambient temperature and present hydrogen bonding interactions. On the other hand, copolymers with IBOA content lower than 50 wt-% present glass transitions above room temperature together with the absence of hydrogen bonding.

CONCLUSIONS

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

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

DECLARATION OF COMPETING INTEREST

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

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    b) The thermograms of the crosslinked homopolymers, poly(IsoBA) and poly(IBOA), and of one of the crosslinked poly(IBOA-co-IsoBA) (80 wt-% IBOA) were reprinted with permission from Ref. 13a. Copyright (2018) by Elsevier Science Ltd. (License Number 4913710611514; License date Sep 21, 2020.

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