



A description of the physical ageing and annealing processes in poly (*N*-vinyl carbazole) using differential scanning calorimetry and two-dimensional correlation mapping analysis

Abdul Ghaffar Al Lafi¹ · Saraa Mousa¹ · Ghina Alssayes¹

Received: 13 September 2023 / Accepted: 16 June 2024 / Published online: 4 July 2024
© Akadémiai Kiadó, Budapest, Hungary 2024

Abstract

Both physical ageing and annealing processes have a remarkable effect on mechanical properties of polymers. In the present work, the physical ageing and annealing processes of poly (*N*-vinyl carbazole) (PNVC), which encompasses phase separation on purification and thermal annealing, have been followed by differential scanning calorimetry (DSC) at different temperatures. The thermal responses were analysed by both generalized two-dimensional correlation mapping (2D-CM) and multiple-perturbation 2D correlation mapping. The asynchronous correlation cross-peak at (233, 211) °C was a measure of the phase separation of the two stereoisomers that contributed to each process. Its intensity was a measure of the effect of holding time on the phase separation, and this was decreased with increasing the holding temperature, which indicated that the occurrence of phase separation was faster at higher holding temperature. The negative values of the correlation peaks indicated that the two relaxation processes changed on the opposite direction. A step change in the correlation intensity with a reflection temperature around 240 °C was observed. The later temperature is interestingly, consistent with the lower critical solution temperature of PNVC reported elsewhere. 2D-CM and its valuable tools provide new routines for DSC thermal responses analysis to extract useful information from complicated polymer systems.

Keywords Physical ageing · Annealing · Differential scanning calorimetry · Poly (*N*-vinyl carbazole) · Tacticity · Two-dimensional correlation mapping

Introduction

Owing to its unusual electrical properties, easiness of polymerization by several routes, interesting morphological characteristics and solution properties, poly (*N*-vinyl carbazole) (PNVC) has captured the focus of attention of current research [1, 2]. It has been shown recently that purification of the as-received polymer and/or thermally annealing it above 275 °C introduced another glass transition (T_g). It was suggested that liquid–liquid phase separation occurred and is driven by the differences in solubility of two stereoisomers, isotactic-rich segments from a matrix, which was predominantly atactic [3]. Further study by two-dimensional Fourier

transform infrared correlation spectroscopy (2D-COS-FTIR) showed that PNVC consisted of polymer chains, some of which was syndiotactic and others isotactic. The predominantly isotactic sequences were insoluble and separate on thermal annealing into two phases with different compositions, and as a consequence, two T_g s were observed [4].

Since its establishment, 2D-correlation analysis has found applications in different analytical fields based on vibrational spectroscopies [5–7] and has been developed and extended to other non-vibrational analytical routines [8–11]. In particular, this technique proved to yield useful information when applied to thermal profile of polymers including thermogravimetric [12] and differential scanning calorimetric analysis [13, 14]. Two-dimensional correlation mapping has been applied to DSC (2D-CM-DSC) to investigate the calorimetric glass transition of polymers and their blends, in which the elucidation potential of the 2D correlation analysis manifested itself by resolving the overlapped glass transitions of polystyrene (PS) and poly(methyl methacrylate) (PMMA) blends [14]. 2D-CM-DSC has been also utilized to examine the heat flow

✉ Abdul Ghaffar Al Lafi
cscientific9@aec.org.sy

¹ Polymer Chemistry Division, Department of Chemistry, Atomic Energy Commission, P.O. Box 6091, Damascus, Syrian Arab Republic

responses of sulfonated poly(ether ether ketone) (sPEEK) films employing two perturbations, i.e. ion exchange capacity and cross-linking density, and two types of loosely bound water within the structure of cross-linked sPEEK were identified [15]. In addition, 2D-CM-DSC has been applied to analyse DSC rate–time data of poly(ether ether ketone) (PEEK), and provided evidence that the fractional n values obtained by the classical Avrami equation, were consistent with the existence of two processes, primary and secondary crystallization. The later was shown to proceed at early stage of primary crystallization [16]. Moreover, 2D-CM-DSC has been conducted to correlate data from different DSC dynamic measurements and extract information related to the origin of multiple melting behaviour of PEEK, which was attributed to the presence of two different crystal types [9].

However, the application of this technique to physical ageing and annealing processes has not been visited yet. Physical ageing is the relaxation of glasses towards the extrapolated mobile liquid state at temperatures close to but below the glass transition temperature. It can be followed experimentally from the size of an endothermic peak, which develops at the glass transition temperature in heating aged samples in a calorimeter. The presence of ageing indicates that the transition is associated with a glass relaxation process [17]. On the other hand, thermal annealing above T_g has been reported to increase the polymer's ability to crystallize [1, 18].

Both processes are reversible, such that if the material that has experienced physical ageing/annealing is raised to a temperature above its T_g /annealing temperature and then rapidly quenched, the effects of ageing/annealing that have occurred previously are removed regardless of the time frame over which they have occurred. Moreover, both processes have a measurable effect on mechanical properties. Physical ageing increases the yield stress, tensile and flexural module progressively, while the fracture toughness, impact strength and compliance decrease [19, 20]. Annealing, on the other hand, has been reported to produce increased values of elongation at break, tensile and yield strength, and yield strain while at the same time Young's modulus was shown to decrease [21, 22].

In the present work, both physical ageing and annealing processes of PNVC, which encompasses phase separation on purification and thermal annealing, have been tracked by DSC at different temperatures. The thermal responses were analysed by 2D-CM, and the overall results were explained based on the underlining physics of the studied processes.

Experimental

Materials and sample preparation

Poly (*N*-vinyl carbazole) (PNVC) in the form of powder was obtained from Sigma-Aldrich Co, Germany. It was

labelled as having a density of 1200 kg m^{-3} , a melting point of $300 \text{ }^\circ\text{C}$, a glass transition of $220 \text{ }^\circ\text{C}$ and an average mass molecular weight of 1100 kg mol^{-1} . Two types of PNVC samples were used in this study. In the first type, PNVC was purified by repeating precipitation from chloroform/methanol under vigorous stirring, and dried in vacuum at $110 \text{ }^\circ\text{C}$ to remove residual solvent. In the second type, PNVC as received was dried at $110 \text{ }^\circ\text{C}$ for several hours.

DSC measurements

A differential scanning calorimeter (Perkin-Elmer model DSC-2) interfaced to a PC Computer was utilized. Measurements were taken at a sensitivity of 20 mW , in flowing nitrogen of $20 \text{ cm}^3 \text{ min}^{-1}$. Temperature and enthalpy calibrations were made with ultra-pure metal standards: indium [melting point (mp): $156.63 \text{ }^\circ\text{C}$, $\Delta H = 29.2 \text{ J g}^{-1}$], tin (mp: $231.91 \text{ }^\circ\text{C}$) and lead (mp: $327.50 \text{ }^\circ\text{C}$). A baseline was established for the instrument using two empty aluminium DSC pans and subtracted from the heat flow-temperature response. Samples of mass $15 \pm 3 \text{ mg}$ were sealed in DSC aluminium pans and the heating scan was recorded from 120 to $270 \text{ }^\circ\text{C}$ at $40 \text{ }^\circ\text{C min}^{-1}$. For the physical ageing experiment, the sample was held a temperature of 200 or $220 \text{ }^\circ\text{C}$ for predetermined time ranged from 30 to 960 min . After that the sample was cooled at $320 \text{ }^\circ\text{C min}^{-1}$ and the heating profile was recorded. A quenched line was recorded by holding PNVC sample at $250 \text{ }^\circ\text{C}$ for 2 min and then cooling the calorimeter at the fastest cooling rate, i.e. at $320 \text{ }^\circ\text{C min}^{-1}$. The quenched sample was then scanned over the temperature range from 120 to $270 \text{ }^\circ\text{C}$ at a heating rate of $40 \text{ }^\circ\text{C min}^{-1}$.

Two-dimensional correlation mapping (2D-CM) analysis

The DSC heat flow–temperature data were pretreated according to the methods described elsewhere with some modifications [9, 15, 16]. All DSC curves were baseline corrected, smoothed with a Savitzky–Golay function (a second-order polynomial and 15 points) and finally, normalized based on sample mass. All thermal responses were first corrected by subtracting the corresponding quenched line, and the overall data were arranged with increasing perturbation; time of ageing or annealing at the corresponding temperatures.

The 2D-Shige version 1.3 software (Shigeaki Morita, Kwansai-Gakuin University, 2004–2005), which is based on the algorithm developed by Noda [23–25], was utilized to compute and visualize 2D-graphs. Sets of data were expressed as a matrix wherein each row is consisted of the heat flow at a given temperature, and each column includes the heat flow at a specific perturbation for different

temperatures. The reference DSC curve was selected as the heat flow response related to the highest perturbation.

Results and discussion

Physical ageing and annealing processes: general observations

It has been reported that high molecular weight PNVC shows a single glass transition temperature (T_g) on the first heating scan, but progressively develops two after purification or after heat treatments [3]. Figure 1 displays an example of the DSC curve for the physically aged purified PNVC samples for 120 min at 5–10 °C below each T_g . Holding at 200 °C generated significant amounts of ageing in the lower transition, as revealed by the large increase in the endothermic peak in Fig. 2a. On the other hand, holding at 220 °C only enabled the higher transition to age; see Fig. 2b. Clearly while the two transitions relaxed towards the mobile liquid on physical ageing, they appeared to perform individually of one another and suggested that two separate and distinct glasses were present where the raw sample demonstrated one.

The areas under the endothermic peak were used as a measure of the rate, at which physical ageing proceeds, see Fig. 2c. The slopes were 0.028 ($R^2 = 0.910$) and 0.002 ($R^2 = 0.992$) for ageing at 200 and 220 °C, respectively. It is well known that the rate of physical ageing is governed by the molecular weight of the relaxed chains, and the proximity of the application temperature to the T_g of the polymer [26, 27]. The reduction in free volume

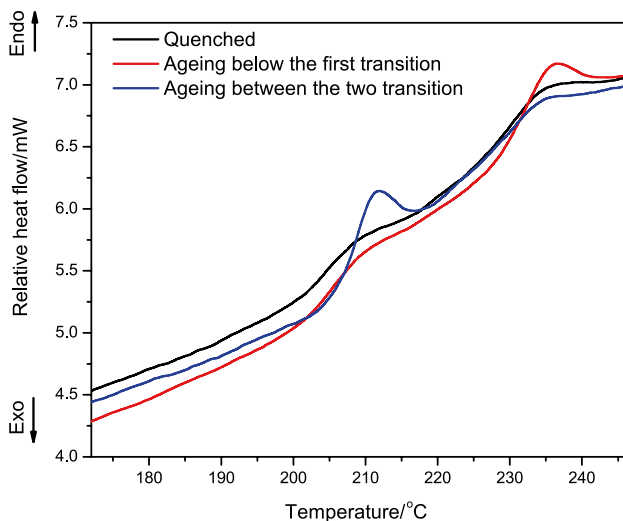


Fig. 1 DSC profiles for purified PNVC samples after holding for 120 min at 200 and 220 °C, compared to the quenched line. Heating rate is 40 °C min⁻¹

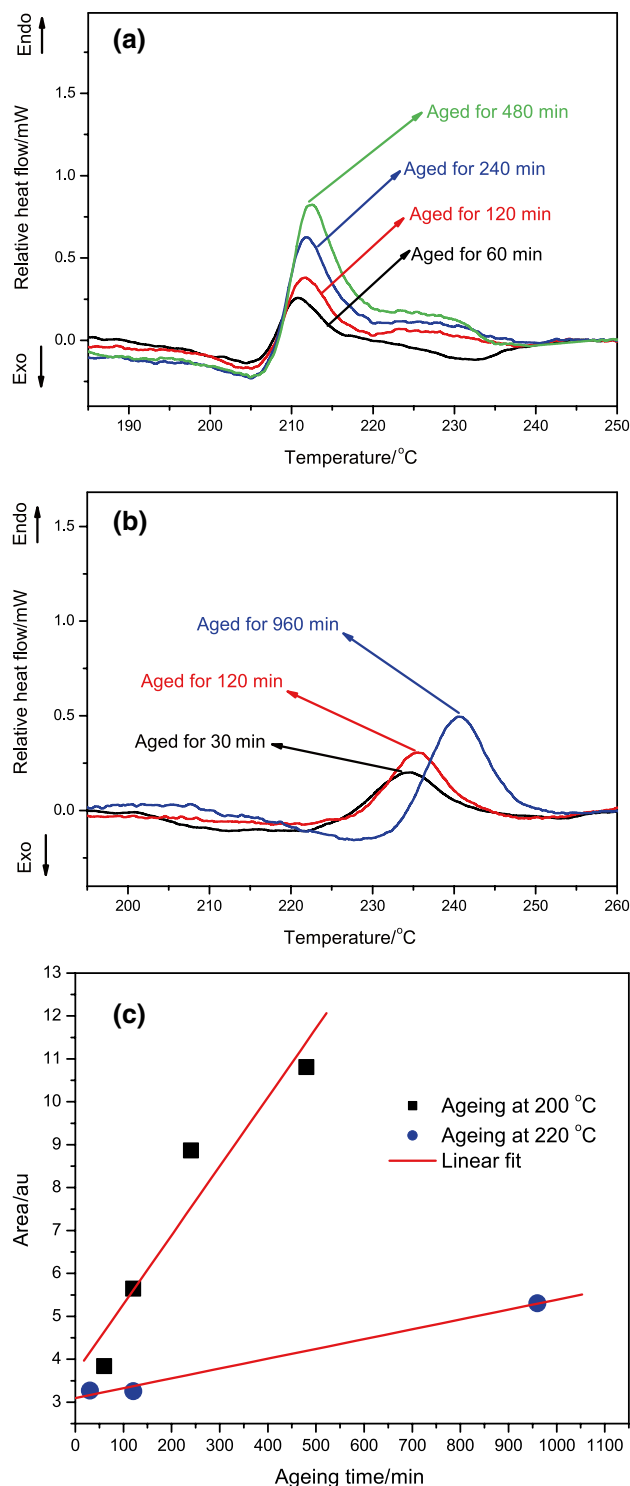


Fig. 2 Enthalpic relaxation in purified PNVC sample **a** below the lower transition and **b** between the two transitions, after subtracting the quenched line. Heating rate is 40 °C min⁻¹. **c** A plot of the area under the endothermic peaks as a function of ageing time

accompanying physical ageing requires some degree of mobility at a molecular level. Lower molecular weight polymers and closer ageing temperature to the T_g , reduces chains entanglement and therefore increases the degree of mobility and elevates the rate of ageing. Similar holding temperatures were chosen for both transitions, i.e. 15 °C below each T_g ; thus, the difference in physical ageing rate could be readily attributed to change in the molecular weight of the relaxed chains.

Figure 3 demonstrates an example of the DSC curve for the thermally annealed as-received PNVC samples for different times and temperatures as indicated. It was clear that annealing above T_g resulted in two T_g s, the lower of which was decreasing with decreasing annealing temperature or time.

2D-CM-DSC analysis

2D-CM methods allow obtaining information regarding the influence of various factors on the studied systems. It is possible to study the effect of one factor or several factors at the same time. This is important in complex systems/processes as 2D-CM techniques facilitate obtaining the information of interest. In the current work, the generalized 2D-CM was applied to obtain information related to the effects of ageing/annealing time on the DSC profile of PNVC. After that, the hybrid 2D-CM was applied to extract information related to the effects of ageing/annealing temperatures. Finally, the multiple-perturbation 2D-CM concept was used to probe the effects of both time and temperature on both processes ageing and annealing.

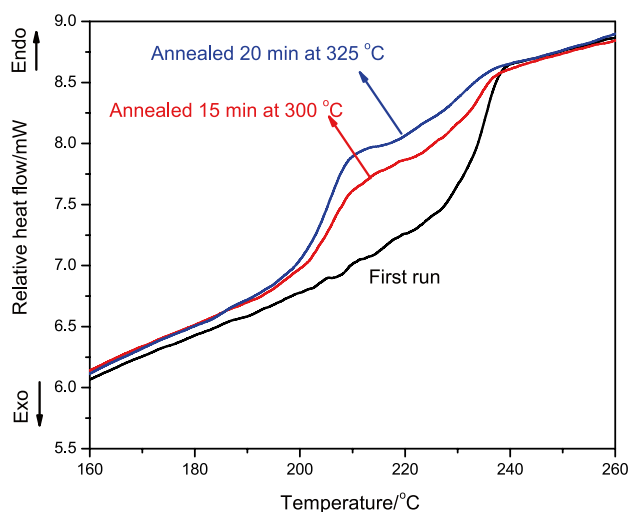


Fig. 3 DSC profiles for as-received PNVC samples after annealing as indicated, compared to the first scan. Heating rate is 40 °C min⁻¹

Ageing below the lower transition

Figure 4 shows the 2D-CM-DSC heat flow responses of purified PNVC sample, which had been aged for various periods at a temperature below the lower T_g , i.e. at 200 °C. The synchronous map, shown in Fig. 4a, exhibits a characteristic angel pattern, comprising two positive auto-peaks at 209 and 214 °C, correlating to each other with two negative cross-peaks at (214, 209) and (209, 214) °C. The auto-peak at 209 °C was markedly large compared to the other auto-peak at 214 °C. The asymmetry of the angel pattern results from the difference in activation energy and the number as well as molecular weight of the contributed chains in the two relaxation processes, which may indicate different types of tacticity of the relaxed chains. The maximum heat flow of the two auto-peaks was used to define the onset and the end temperature of the peak, at 209 and 214 °C, respectively. The asynchronous map, Fig. 4b, displays the characteristic distorted butterfly pattern, containing a pair of elongated cross-peaks of opposing signs situated very close to the diagonal and near the stronger auto-peak side, i.e. the peak at 209 °C. Next to these elongated cross-peaks and relatively away from the diagonal, are another set of lower intensity cross-peaks. The patterns spotted in both synchronous and asynchronous maps are characteristic of peaks shift paired with an intensity change [28]. The direction of the change is verified by the signs of the asynchronous cross-peaks within the butterfly cluster, as demonstrated by Noda and Ozaki [5]. The elongated cross-peak over the diagonal is negative, and that under the diagonal is positive, which suggests that the peak position is moving from right to left along the horizontal axis of the 2D-CM map and from top to bottom along the vertical axis. In other words, increasing the ageing time increased the number/length of relaxed chains or even enabled the different stereo-chemical chains to relax and contributed to the peak of ageing. This was consistent with the nature of physical ageing process [19, 20] and the

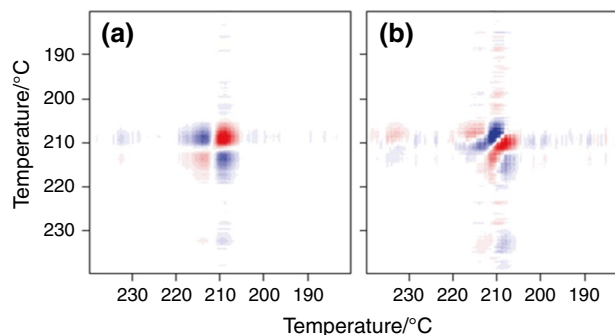


Fig. 4 The 2D-CM-DSC heat flow responses of PNVC sample undergoing physical ageing below the lower transition, i.e. at 200 °C. **a** The synchronous and **b** the asynchronous maps

increase of evolved relaxation enthalpy with increasing ageing time as depicted in Fig. 2.

In addition, there was a cross-peak located at (233, 209) °C, which had a negative sign in the synchronous map and a positive sign in the asynchronous map. This indicated that the two relaxation processes occurred on the opposite direction of each other, and that the process at 209 °C proceeded faster or before that at 233 °C. It should be noted that there was another low intensity cross-peak at (233, 214) °C, which had a positive sign in the synchronous map and a negative sign in the asynchronous map. This indicated that the two relaxation processes occurred on the same direction; increasing in intensity with increasing ageing time, and that the process at 214 °C proceeded faster or before that at 233 °C. These results confirmed the observed peak shift paired with intensity change. The intensity of the starter peak at 209 °C was reduced and shifted to 214 °C, which was progressively developed with increasing ageing time. As the temperature at 233 °C corresponded to the higher T_g, the 2D-CM showed that there was some ageing occurring on the higher T_g. This implied that the chains relaxed at the lower temperature were the shortest or the lowest in molecular weight. In other word, they could be assigned to the lower T_g of stereo-blocks form of the polymer, i.e. the isotactic form or more accurately the atactic form of the polymer with more isotactic contents. The second explanation was more relevant and accepted as the T_gs values of the stereo-blocks form of PNVC have been reported at 126, 227 and 276 °C corresponding to isotactic, atactic and syndiotactic forms, respectively [1, 29]. All observed temperatures were in the range of atactic stereo-blocks, and the ageing temperature at 200 °C was suitable to age the fraction of atactic stereo-block.

The sequential order of peaks changes followed the order: 214(↑) → 209(↓) → 233(↑) °C. Both processes at 214 °C and 233 °C increased and the process at 209 °C decreased. It was suggested that the process at 209 °C represent an intermediate state, which consisted of unstable solid solution of different stereo-blocks of the polymer. The ageing for extended times allowed some chains to have sufficient energy to relax and two phases separated, both of which are syndiotactic rich but they have different syndiotactic contents or configurations, i.e. 2:1 or 4:1 or all Trans helices [30].

Ageing between the two transitions

Figure 5 shows the 2D-CM-DSC heat flow responses of PNVC sample, which had been aged for various periods at a temperature below the higher T_g but above the lower one, i.e. at 220 °C. The synchronous map, shown in Fig. 5a, exhibits a characteristic angel pattern, comprising two positive auto-peaks, one of which is appeared at 242 °C and the other centred at 237 °C. In addition,

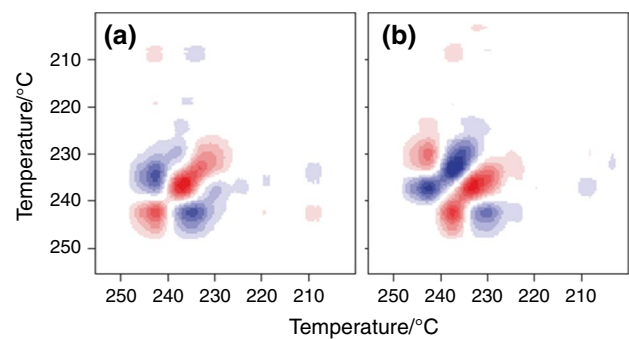


Fig. 5 The 2D-CM-DSC heat flow responses of PNVC sample undergoing physical ageing between the two transitions, i.e. at 220 °C. **a** The synchronous and **b** the asynchronous maps

two negative cross-peaks were observed at (242, 237) and (237, 242) °C. The auto-peak at 237 °C was larger compared to the other auto-peak at 242 °C. These indicated that the process at 237 °C changed in the opposite direction compared to the process at 242 °C. The asymmetry of the angel pattern resulted from the differences in activation energy and the numbers as well as molecular weights of the contributed chains in the two relaxation processes, which may signify different types of tacticity of the relaxation processes. The maximum heat flow of the two auto-peaks was used to identify the temperature of the initial and final peak, at 237 and 242 °C, respectively. The asynchronous map, shown in Fig. 5b, displays the characteristic distorted butterfly pattern, involving a pair of elongated cross-peaks of opposing signs placed very adjacent to the diagonal and near the stronger auto-peak side, i.e. the peak at 237 °C. Next to these elongated cross-peaks and slightly away from the diagonal, are another set of lower intensity cross-peaks. The patterns observed in both synchronous and asynchronous maps are representative of peaks shift paired with an intensity change. The elongated cross-peak above the diagonal is negative, and that below the diagonal is positive, which designates that the peak position is shifting from right to left along the horizontal axis of the 2D-CM map and from top to bottom along the vertical axis. In other words, increasing the ageing time increased the number/length of relaxed chains or even enabled the different stereo-chemical chains to relax and contributed to the peak of ageing. This was consistent with the nature of physical ageing process and the increase of evolved relaxation enthalpy with increasing ageing time as depicted in Fig. 2. These results indicated similar behaviour with the previous results of Fig. 4, but with higher set of temperatures, i.e. at 237 and 242 °C. Moreover, the ageing temperature at 220 °C was suitable to age the fraction of atactic stereo-block, i.e. 5–10 °C below the T_g of atactic PNVC. This was also in accordance with the conclusion made in the literature, such that

the insolubility of the syndiotactic dyads in the isotactic dyads enhanced with rising temperature and consequently the phases which relaxed retain a different tacticity [3].

In summary, similar conclusions were made by analysing the two ageing processes using the concept of 2D-CM, which confirmed the applicability of this routine to study ageing. Purified PNVC represents a solid solution of the different stereo-blocks, the composition of which was temperature and time dependent.

Annealing above the higher transition

Figure 6 shows the 2D-CM-DSC heat flow responses of as-received PNVC sample, which had been annealed for various periods at a temperature of 300 °C. The synchronous map, Fig. 6a, shows two positive auto-peaks at 211 and 233 °C correlating to each other with two negative cross-peaks at (233, 211) and (211, 233) °C. The auto-peak at 211 °C was larger than the other auto-peak at 233 °C. These indicated that the process at 211 °C changed in the opposite direction compared to the other process at 233 °C. The asynchronous map, shown in Fig. 6b, shows a negative cross-peak situated at (233, 211) °C. According to Noda rule, the process at 233 °C proceeded faster or before that at 211 °C.

Figure 7 shows the 2D-CM-DSC heat flow responses of as-received PNVC sample, which had been annealed for various periods at a temperature of 325 °C. The synchronous map, shown in Fig. 7a, shows two positive auto-peaks at 211 and 233 °C correlating to each other with two negative cross-peaks at (233, 211) and (211, 233) °C. The auto-peak at 211 °C was larger compared to the other auto-peak at 233 °C. These indicated that the process at 211 °C changed in the opposite direction compared to the other process at 233 °C. The asynchronous map, shown in Fig. 7b, shows a negative cross-peak located at (233, 211) °C. According to Noda rule, the process at 233 °C proceeded faster or before that at 211 °C.

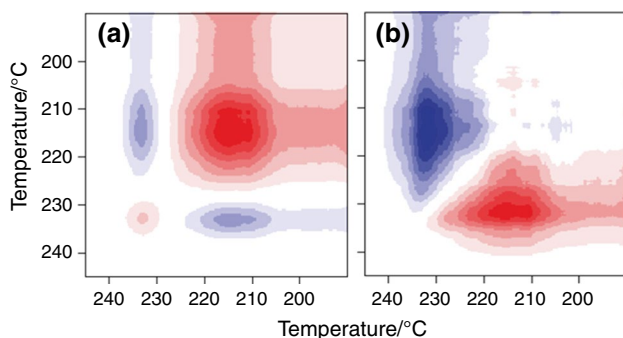


Fig. 6 2D-M-DSC for the annealing process at 300 °C; the synchronous **a** and the asynchronous **b** maps

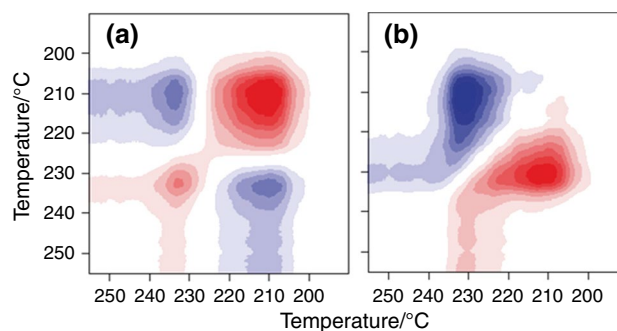


Fig. 7 2D-M-DSC for the annealing process at 325 °C; the synchronous **a** and the asynchronous **b** maps

Discussion

Statistical calculations and NMR studies have shown that syndiotactic sequences of PNVC are predominant by the all-trans form, which is the most stable conformation among others such as 2/1 and 4/1 arrangements, provided that steric interactions are presumed to be prevalent over all other possible interactions [30]. On the other hand, isotactic sequences of PNVC are dominated by the 3/1 helical form. The portion of isotactic and syndiotactic sequences are approximately equal for samples of ‘isotactic-rich’ PNVC, while for the ‘syndiotactic-rich’ samples of PNVC the syndiotactic fraction has risen to about 75%. Moreover, the observation of two Tgs in a miscible polymer blend or polymer solution has been already done and it was concluded that two transitions did not indicate immiscibility [31]. In the present work, it is reported the same case but with one polymer which possesses different tacticity due to the bulky side groups.

It seems that the polymer existed in non-equilibrium state with respect to stereo-chemical composition due to the bulky carbazole side groups. Holding the polymer at temperatures above its multiple Tgs for extended time allowed the different chains to relax and consequently two miscible atactic portions of the polymer resulted. These have Tgs at 211 and 233 °C and could be both regarded as isotactic-rich phase. The only difference between them is the length of the chains that contributed to the process.

Hybrid correlation 2D-CM-DSC approach

To survey the similarity and/or difference between two systems or processes, hybrid 2D correlation spectroscopy has been documented and tested [32–34]. In the present work, the data reported in both Figs. 4 and 5 were collected under the same perturbation (ageing time) but different conditions (different ageing temperature). Therefore, a case III hybrid correlation is met [32] and hybrid 2D correlation maps could be constructed.

Figure 8a displays the synchronous hybrid 2D correlation map built from the ageing time-dependent DSC profiles of purified PNVC aged at two temperatures, namely at 200 and 220 °C. A large asymmetry of the synchronous hybrid 2D correlation map was perceived, such that the 2D peaks shifted to the higher temperature side. This indicates that the two studied processes involved the relaxations of different stereo-block of the polymer that have different molecular weight or different free volume/mobility and they stabilized by changing the tacticity to more syndiotactic-rich stereo-block. This was in contrary with the literature, as it has been reported that the isotactic form is more thermally stable in most polymers [35, 36]. Therefore, the observed results were attributed to changes in configuration of PNVC from p-PNVC or exciplex to f-PNVC or excimer configurations. The later has a higher glass transition temperature [4, 37].

There were two cross-peaks of lower intensity, one of which was positive correlated the peaks at (233, 242) °C and the other was negative that correlated the peaks at (233, 233) °C. This indicated the process at 233 °C on ageing at 200 °C changed on the same direction with process at 242 °C on ageing at 220 °C. As the process at 233 °C decreased on the first ageing, thus the process at 242 °C decreased on the second ageing. Ultimately, all processes would transform to the process at 209 °C, which represent the T_g of the most stable isotactic-rich form of the polymer. It was also interesting to observe the negative cross-peak at (233, 233) °C which indicated that this process was the least affected in both ageing processes as it increased in one while decreased in the other one, to keep the composition of the polymer at the most equilibrated and stable state. In the asynchronous hybrid 2D-CM-DSC map in Fig. 8b, new peaks appeared at 230 and 237 °C. It was noted that the peak at 233 °C split into two peaks at 230 and 237 °C. This indicated the presence of intermediate state.

Ageing at 200 °C increased the intensity of the peak at 214 °C, which was consistent with the analysis of 2D-MC-DSC in Fig. 4. The positive peaks at (214, 237) and (234,

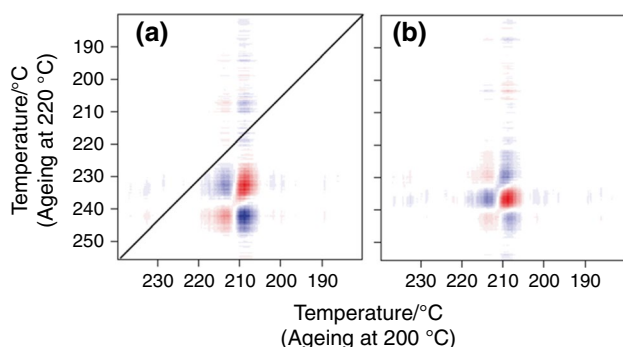


Fig. 8 The hybrid 2D-M-DSC for the physical ageing: **a** the synchronous and **b** the asynchronous maps

237) °C indicated that ageing at 220 °C caused the peak at 237 °C to change in the same direction with the peaks at 214 and 234 °C in carrying out the ageing at 200 °C. Thus, the peak at 237 °C should increase in intensity, which was in contrary to the analysis of 2D-CM-DSC in Fig. 5. The same conclusions were obtained by analysing the negative correlation peaks at (214, 242) and (230, 242) °C.

It is suggested that the second ageing temperature caused two processes to occur simultaneously: ageing of another atactic stereo-block, which had more syndiotactic content, and crystallization of parts of the polymer. The contribution of the later process was dominant and caused the T_g to shift to higher temperature.

Multiple-perturbation 2D-CM-DSC approach

As shown earlier in this article, both ageing and annealing depend upon both the holding temperature and the time during which the sample kept at that temperature. 2D-CM method, namely multiple-perturbation 2D correlation mapping (MP2D-CM), enables the extraction of information related to each factor. MP2D-CM was first suggested to explore the mixed dynamic responses of a system that has been disturbed by more than one type of perturbation [38]. It has been applied successfully to probe the effects of both cross-linking density and ion exchange capacity on the water contents and type present in sulfonated poly (ether ether ketone) samples by the analysis of their DSC curves [15].

As can be seen from Fig. 9, the partial asynchronous correlation intensities between the signals of the two relaxation processes, i.e. the correlation peak at (233, 211) °C, decreased with increasing the holding temperature. The asynchronous correlation was a measure of the number of the chains and their molecular weight that contributed to each relaxation process, and they were measured by the first glass transition, i.e. at 211 °C.

The negative values of the correlation peaks indicated that the two relaxation processes changed on the opposite direction. The decrease in the correlation values indicated that the rate of the process decreased with increasing the holding temperature.

From the 1D DSC profiles, it was observed that the process at 211 °C increased with annealing time while the other process decreased. There was also a shift to higher temperatures with both processes on increasing annealing time, but the shift was more pronounced in the higher process. The presence of cross correlation peaks at 242 °C in the 2D maps was consistent with this.

The results of Bai et al. [39] indicated that the lower molecular weight fractions of PNVC did not develop a liquid crystalline phase, while the samples of sufficiently high molecular weight formed a mesophase at temperatures above the glass transition. Accordingly, the process

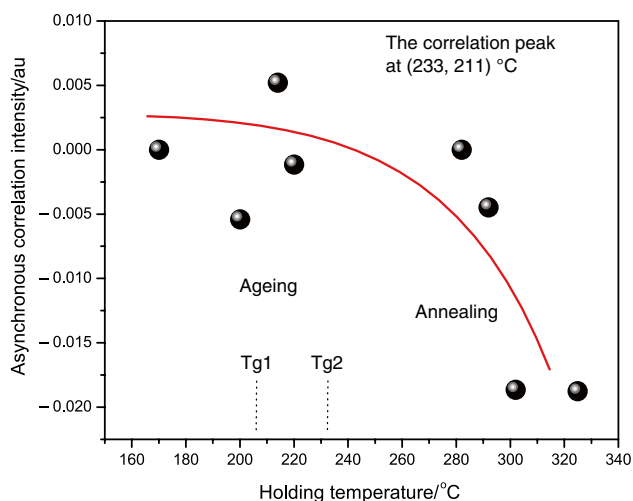


Fig. 9 The asynchronous correlation intensities between the two types of relaxation processes depending on holding temperature. Line is guided for the eyes

at 211 °C represents the low molecular fraction of the polymer and the stereo-chemical form that does not crystallize or at least form crystalline liquid (isotactic rich). The second process on the other hand, represent the higher molecular weight fraction of the polymer and as this fraction crystallize or form crystalline liquid or at least undergoes molecular orientation, the temperature shifts to higher values. That is why it should decrease with increasing annealing time. The 2D-DSC analysis showed that the decrease in the process at 233 °C occurred before the increase in the process at 211 °C. This implied that some part of the polymer chains relaxed and contributed to the new process at 242 °C while the other were unstable at the annealing temperature so they separated and contributed to the lower relaxation process at 211 °C. This confirmed that the higher process represents different stereoform of the polymer mostly syndiotactic rich. The conclusion reported that thermal annealing caused phase separation is consistent with this assignment.

The asynchronous correlation at (233, 211) °C was a measure of the phase separation of the two stereoforms that contributed to each process. Its intensity is a measure of the effect of holding time on the phase separation, and this was decreased with increasing the holding temperature which indicated that the occurrence of phase separations was faster at higher holding temperature. The negative values of the correlation peaks indicated that the two relaxation processes changed on the opposite direction. The decrease in the correlation values indicated that the rate of the process decreases with increasing the holding temperature due to the decreases in the number of relaxed chains. As shown in Fig. 9, there was a step change in the correlation intensity with a reflection temperature around

240 °C. Interestingly, this value was consistent with the lower critical solution temperature (LCST) of PNVC which has been reported elsewhere.

It suggested that the relaxation at the higher temperature involved the combination of many processes: diffusion of the short length chains out and their relaxation, rearrangement of the chains that exhibit more entanglement and their stereo-chemical isomerization to more stable form. All of these resulted in phase separation and the presence of two Tg processes that showed ageing separately at different holding temperatures.

The samples annealed above the higher Tg have higher activation energy for segmental arrangement of polymer chains in order for crystal formation to proceed; therefore, they should exhibit the features of crystallinity.

Conclusions

2D-CM has been demonstrated as a suitable analysis routine for the thermal responses of both physical ageing and annealing processes of PNVC. The 2D-CM results were consistent with the underlining physics of the studied processes. Hybrid 2D-CM analysis enabled the comparison between ageing of the two observed glass transitions, and indicated that the two studied processes involved the relaxations of different stereo-block of the polymer that have different molecular weight or different free volume/mobility and they stabilized by changing the tacticity to more isotactic-rich stereo-block. The multiple-perturbation 2D correlation mapping approach helped to extract information related to the effects of both the holding temperature and the time during which the sample kept at that temperature on the tacticity of the polymer. In particular, the negative asynchronous correlation cross-peak at (233, 211) °C decreased with increasing the holding temperature/time which indicated that phase separation was tacticity dependent. In addition, the plot of the asynchronous correlation intensity against temperature had a reflection point around 240 °C, which was consistent with the LCST of PNVC. 2D-CM provides multiple routines for DSC thermal responses analysis and is a powerful tool for thermal analysis of polymers.

Acknowledgements The authors acknowledge the financial support of the Atomic Energy Commission of Syria during the tenure of the work.

Author contributions Abdul G. Al Lafi contributed to the supervision, conceptualization, and writing—original draft; Saraa Mousa performed the formal analysis and investigation; G. Alsayes was involved in the methodology and visualization.

Funding This study was funded by Atomic Energy Commission of Syria (AECS).

Declarations

Conflict of interest The authors have no conflict of interest to declare that are relevant to the content of this article.

References

- Penwell RC, Ganguly BN, Smith TW. Poly(*N*-vinylcarbazole): a selective review of its polymerization, structure, properties, and electrical characteristics. *J Polym Sci Macromol Rev.* 1978;13:63–160. <https://doi.org/10.1002/pol.1978.230130102>.
- Schildknecht CE. Vinyl and related polymers. Hoboken: Wiley; 1952.
- Al-Lafi AG, Hay JN. Stereo-chemical contributions to the glass transition and liquid–liquid phase separation in high molecular weight poly(*N*-vinyl carbazole). *RSC Adv.* 2016;6:29326–33. <https://doi.org/10.1039/c6ra00097e>.
- Al-Lafi AG, Hay JN. 2D-COS-FTIR analysis of high molecular weight poly (*N*-vinyl carbazole) undergoing phase separation on purification and thermal annealing. *J Mol Struct.* 2019;1175:152–62. <https://doi.org/10.1016/j.molstruc.2018.07.077>.
- Noda I, Ozaki Y. Two-dimensional correlation spectroscopy: applications in vibrational and optical spectroscopy. Chichester: Wiley; 2004.
- Al-Lafi AG. FTIR spectroscopic analysis of ion irradiated poly (ether ether ketone). *Polym Degrad Stab.* 2014;105:122–33. <https://doi.org/10.1016/j.polymdegradstab.2014.04.005>.
- Noda I. Generalized two-dimensional correlation method applicable to infrared, Raman, and other types of spectroscopy. *Appl Spectrosc.* 1993;47:1329–36. <https://doi.org/10.1366/0003702934067694>.
- Al-Lafi AG, Mougrabya MA, Shehada O. On the application of two-dimensional correlation spectroscopy to analyze X-ray photoelectron spectroscopic data. *J Polym Res.* 2022;29:11. <https://doi.org/10.1007/s10965-021-02857-8>.
- Al-Lafi AG, Alsayes G. Interpretation of multiple melting behaviour in poly (ether ether ketone) revisited: two-dimensional correlation mapping approach. *J Therm Anal Calorim.* 2022;147:6219–26. <https://doi.org/10.1007/s10973-021-10964-3>.
- Al-Lafi AG, Rihawy MS. RBS and PIXE data analysis by two dimensional correlation mapping techniques: on the effects of ion irradiation and sulfonation on poly(ether ether ketone) membranes. *X-Ray Spectrom.* 2021;50(2):121–33. <https://doi.org/10.1002/xrs.3206>.
- Al-Lafi AG, Alzier A, Allaf AW. Wide angle X-ray diffraction patterns and 2D-correlation spectroscopy of crystallization in proton irradiated poly(ether ether ketone). *Heliyon.* 2021;7: e07306. <https://doi.org/10.1016/j.heliyon.2021.e07306>.
- Sui HL, Liu XY, Zhong FC, Li XY, Jua X. A study of radiation effects on polyester urethane using two-dimensional correlation analysis based on thermogravimetric data. *Polym Degrad Stab.* 2013;98:255–60. <https://doi.org/10.1016/j.polymdegradstab.2012.10.003>.
- He X, Cai S, Yu H, Chen Q, Hou H. DSC differential spectrum applied in the study of hydrogen bonding interaction in aqueous solution. *Int J Polym Anal Charact.* 2014;19:141–50. <https://doi.org/10.1080/1023666X.2014.872882>.
- Pin J-M, Anstey A, Anstey A, Park CB, Lee PC. Exploration of polymer calorimetric glass transition phenomenology by two-dimensional correlation analysis. *Macromolecules.* 2021;54:473–87. <https://doi.org/10.1021/acs.macromol.0c01819>.
- Al-Lafi AG, Hay JN. State of the water in crosslinked sulfonated poly(ether ether ketone). Two-dimensional differential scanning calorimetry correlation mapping. *Thermochim Acta.* 2015;612:63–9. <https://doi.org/10.1016/j.tca.2015.05.008>.
- Al-Lafi AG, Hay JN. The isothermal crystallization of poly(ether ether ketone) by two-dimensional differential scanning calorimetry correlation mapping. *J Appl Polym Sci.* 2017;134(4):44378. <https://doi.org/10.1002/app.44378>.
- Cowie JMG. Polymers: chemistry and physics of modern materials. 2nd ed. London: Chapman Hall; 1991.
- Kimura A, Yoshimoto S, Akana Y, Hirata H, Kusabayashi S, Mikawa H, Kasai N. Crystallinity of poly-*N*-vinylcarbazole. *J Polym Sci Part A2 Polym Phys.* 1970;8:643–8.
- Hay JN. The physical ageing of amorphous and crystalline polymers. *Pure Appl Chem.* 1995;67:1855–8.
- Atkinson JR, Hay JN, Jenkins MJ. Enthalpic relaxation in semi-crystalline PEEK. *Polymer.* 2002;43:731–5. [https://doi.org/10.1016/S0032-3861\(01\)00668-1](https://doi.org/10.1016/S0032-3861(01)00668-1).
- Von Metzen RP, Stieglitz T. The effects of annealing on mechanical, chemical, and physical properties and structural stability of Parylene C. *Biomed Microdevices.* 2013;15:727–35. <https://doi.org/10.1007/s10544-013-9758-8>.
- Butt J, Bhaskar R. Investigating the effects of annealing on the mechanical properties of FFF-printed thermoplastics. *J Manuf Mater Process.* 2020;4:38–57. <https://doi.org/10.3390/jmmp4020038>.
- Park Y, Jin S, Noda I, Jung YM. Continuing progress in the field of two-dimensional correlation spectroscopy (2D-COS): part III. Versatile applications. *Spectrochim Acta Part A.* 2023;284:121636. <https://doi.org/10.1016/j.saa.2022.121636>.
- Park Y, Jin S, Noda I, Jung YM. Continuing progress in the field of two-dimensional correlation spectroscopy (2D-COS), part II. Recent noteworthy developments. *Spectrochim Acta Part A.* 2023;284:121750. <https://doi.org/10.1016/j.saa.2022.121750>.
- Park Y, Jin S, Noda I, Jung YM. Continuing progress in the field of two-dimensional correlation spectroscopy (2D-COS), part I. Yesterday and today. *Spectrochim Acta Part A.* 2022;281:121573. <https://doi.org/10.1016/j.saa.2022.121573>.
- Priestley RD, Ellison CJ, Broadbelt LJ, Torkelson JM. Structural relaxation of polymer glasses at surfaces, interfaces, and in between. *Science.* 2005;309:456–9. <https://doi.org/10.1126/science.1112217>.
- Minguez R, Barrenetxea L, Solaberrieta E, Lizundia E. A simple approach to understand the physical aging in polymers. *Eur J Phys.* 2019;40:015502. <https://doi.org/10.1088/1361-6404/aaf244>.
- Morita S, Shinzawa H, Noda I, Ozaki Y. Effect of band position shift on moving-window two-dimensional correlation spectroscopy. *J Mol Struct.* 2006;799:16–22.
- Pearson JM. Vinylcarbazole polymers in encyclopedia of polymer science and engineering, vol. 257. New York: Wiley; 1987.
- Mumby SJ, Beevers MS. Electro-optical studies of various stereostructural forms of poly(*N*-vinylcarbazole). *Polymer.* 1989;30:860–5. [https://doi.org/10.1016/0032-3861\(89\)90183-3](https://doi.org/10.1016/0032-3861(89)90183-3).
- Lodge TP, Wood ER, Haley JC. Two calorimetric glass transitions do not necessarily indicate immiscibility: the case of PEO/PMMA. *J Polym Sci Part B Polym Phys.* 2006;44:756–63.
- Wu Y, Jiang J-H, Ozaki Y. A new possibility of generalized two-dimensional correlation spectroscopy: hybrid two-dimensional correlation spectroscopy. *J Phys Chem A.* 2002;106:2422–9.
- Wu Y, Meersman F, Ozaki Y. A novel application of hybrid two-dimensional correlation infrared spectroscopy: exploration of the reversibility of the pressure- and temperature-induced phase separation of Poly(*N*-isopropylacrylamide) and Poly(*N*-isopropylmethacrylamide) in aqueous solution. *Macromolecules.* 2006;39:1182–8.
- Al-Lafi AG. Molecular dynamics in ion-irradiated poly(ether ether ketone) investigated by two-dimensional correlation dielectric

- relaxation spectroscopy. *Polym Adv Technol.* 2014;25:9–15. <https://doi.org/10.1002/pat.3197/pdf>.
35. Worch JC, Prydderch H, Jimaja S, Bexis P, Becker ML, Dove AP. Stereochemical enhancement of polymer properties. *Nat Rev Chem.* 2019;3:514–35. <https://doi.org/10.1038/s41570-019-0117-z>.
36. Chen K, Harris K, Vyazovkin S. Tacticity as a factor contributing to the thermal stability of polystyrene. *Macromol Chem Phys.* 2007;208:2525–32. <https://doi.org/10.1002/macp.200700426>.
37. Claire PdS. Molecular simulation of excimer fluorescence in polystyrene and poly(vinylcarbazole). *J Phys Chem B.* 2006;110:7334–43. <https://doi.org/10.1021/jp056987e>.
38. Shinzawa H, Awa K, Noda I, Ozaki Y. Multiple-perturbation two-dimensional near-infrared correlation study of time-dependent water absorption behavior of cellulose affected by pressure. *Appl Spectrosc.* 2013;67:163–70.
39. Bai Y, Chen X, Wan X, Zhou Q. Study on liquid crystallinity of Poly(*N*-vinylcarbazole). *Chin J Polym Sci.* 2002;20:155–9.

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.